

**Class 2 Permit Modification Requests**

**For the**

**Waste Isolation Pilot Plant  
Carlsbad, New Mexico**

**WIPP HWFP Number NM4890139088-TSDF**

**August 28, 2001**

**Revised**

**September 28, 2001**

|  
|  
|

## TRANSMITTAL LETTER

## Table of Contents

Table of Contents .....	i
Acronyms and Abbreviations .....	ii
Overview of the Permit Modification Request .....	1
Attachment A .....	A-1
Table 1. Class 2 Hazardous Waste Facility Permit Modification .....	A-2
Item 1 Using Composite Headspace Gas Data and Compositing up to 20 Samples .....	A-3
Description .....	A-3
Basis .....	A-3
Discussion .....	A-4
Proposed Revised Permit Text .....	A-9
Item 2 Establishing Safety Conditions for Visual Examination (VE) of Waste Containers ..	A-19
Description .....	A-19
Basis .....	A-19
Discussion .....	A-19
Proposed Revised Permit Text .....	A-22
Item 3 Taking Samples of Headspace Gas through Existing Filter Vent Holes .....	A-24
Description .....	A-24
Basis .....	A-24
Discussion .....	A-24
Proposed Revised Permit Text .....	A-26
Attachment B INFORMATION SUPPORTING ITEM 1 .....	
Attachment C INFORMATION SUPPORTING ITEM 2 .....	
Attachment D INFORMATION SUPPORTING ITEM 3 .....	

## Acronyms and Abbreviations

AEA	Atomic Energy Act
ALARA	As Low As Reasonably Achievable
CBFO	Carlsbad Field Office
DOE	Department of Energy
EPA	Environmental Protection Agency
FR	Federal Register
GC	Gas Chromatography
HWDU	Hazardous Waste Disposal Unit
HWFP	Hazardous Waste Facility Permit
MS	Mass Spectrometry
NMAC	New Mexico Administrative Code
NMED	New Mexico Environment Department
NRC	Nuclear Regulatory Commission
POC	Pipe Overpack Container
PMR	Permit Modification Request
PRQL	Program Required Quantitation Limit
QA	Quality Assurance
QAO	Quality Assurance Objectives
QAPjP	Quality Assurance Project Plan
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
SOP	Standard Operating Procedure
TCLP	Toxicity Characteristic Leaching Procedure
TIC	Tentatively Identified Compound
TRU	Transuranic
TSDF	Treatment, Storage, and Disposal Facility
UCL <sub>90</sub>	Upper 90 Percent Confidence Level
VE	Visual Examination
VOC	Volatile Organic Compound
WAC	Waste Acceptance Criteria
WAP	Waste Analysis Plan
WHB	Waste Handling Building
WIPP	Waste Isolation Pilot Plant
WTS	Westinghouse TRU Solutions
WWIS	WIPP Waste Information System

## Overview of the Permit Modification Request

This document contains a Permit Modification Request (PMR) that includes three (3) items that propose to change the Hazardous Waste Facility Permit (HWFP) at the Waste Isolation Pilot Plant (WIPP) Number NM4890139088-TSDF. This PMR is being submitted by the U.S. Department of Energy (DOE), Carlsbad Field Office (CBFO) and Westinghouse TRU Solutions (WTS), collectively referred to as the Permittee, in accordance with the WIPP HWFP Condition I.B.1. The modifications will improve both efficiency and safety at the generator/storage sites. These changes do not reduce the ability of the Permittee to provide continued protection to human health and the environment.

The requested modifications to the WIPP HWFP and related supporting documents are provided in the following sections of the PMR. The proposed modifications to the text of the WIPP HWFP have been identified using a double underline for new information added and a ~~strikeout~~ font for information proposed for deletion. All direct quotations are indicated by using italicized text.

The following information specifically addresses how compliance with the WIPP HWFP requirement, Permit Condition I.B.1 for submission of this PMR is achieved.

**1. 20.4.1.900 NMAC (incorporating 40 CFR § 270.42(b)(1)(i)) requires the applicant to describe the exact change to be made to the permit conditions and supporting documents referenced by the permit.**

The proposed modification contains three considerations that will allow waste analysis activities required by the WAP to function safely and more efficiently. DOE has submitted these modifications for consideration as follows:

- C Using Composite Headspace Gas Data and Compositing up to 20 Samples
- C Establishing Safety Conditions for Visual Examination (VE) of Waste Containers
- C Taking Samples of Headspace Gas through Existing Filter Vent Holes

The exact changes to the HWFP for each of these items are described in Attachment A.

**2. 20.4.1.900 NMAC (incorporating 40 CFR § 270.42(b)(1)(ii)) requires the applicant to identify that the modification is a Class 2 modification.**

Using Composite Headspace Gas Data and Compositing up to 20 Samples

This PMR item changes the method in which headspace gas samples are handled and analyzed. It allows generator/storage sites to composite individual field samples into a single analytical sample. Because this affects the waste sampling method it is classified under 20.4.1.900 NMAC incorporating 40 CFR 270, Appendix I, as Type B.1.d, "other changes to waste sampling and analysis methods."

Establishing Safety Conditions for Visual Examination (VE) of Waste Containers

This PMR item would allow generator/storage sites to implement safety criteria when randomly selecting containers for VE. The selected containers are used to perform quality control for radiography. Because this affects the quality control portion of the Waste Analysis Plan in the HWFP this is classified under 20.4.1.900 NMAC incorporating 40 CFR 270, Appendix I, as Type B.2.b, “other changes to the analytical quality assurance/control plan.”

#### Taking Samples of Headspace Gas through Existing Filter Vent Holes

This PMR item provides an alternative sampling methodology for generator/storage sites to use in taking headspace gas samples. The method allows sampling through the existing filter vent hole using an airtight sampling device. Because this affects waste sampling methods it is classified under 20.4.1.900 NMAC incorporating 40 CFR 270, Appendix I, as Type B.1.d, “other changes to waste sampling and analysis methods.”

3. **20.4.1.900 NMAC (incorporating 40 CFR § 270.42(b)(1)(iii)) requires the applicant to explain why the modification is needed.**

The basis and discussion relative to the necessity for each of the PMR items are included in Attachment A in the Item-by-Item descriptions.

4. **20.4.1.900 NMAC (incorporating 40 CFR § 270.42 (b)(1)(iv)) requires the applicant to provide the applicable information required by 40 CFR 270.13 through 270.21, 270.62 and 270.63.**

The regulatory crosswalk describes those portions of the permit that are affected by these proposed modifications. Where applicable, regulatory citations in this PMR reference Title 20, Chapter 4, Part 1, New Mexico Administrative Code (NMAC), revised June 14, 2000, incorporating the Code of Federal Regulations, Title 40 (40 CFR 264 and 270).

5. **20.4.1.900 NMAC (incorporating 40 CFR §§ 270.11(d)(1) and 40 CFR 270.30(k)) requires any person signing under paragraph a and b must certify the document in accordance with 20.4.1.900 NMAC.**

The transmittal letter for this PMR contains the signed certification statement in accordance with Module I.F of the WIPP HWFP.

## Regulatory Crosswalk

Regulatory Citation(s) 20.4.1.900 NMAC (incorporating 40 CFR 270)	Regulatory Citation(s) 20.4.1.500 NMAC (incorporating 40 CFR 264)	Description of Requirement	Added or Clarified Information		
			Section of the HWFP or Permit Application	Yes	No
§ 270.13		Contents of Part A permit application	Attachment O, Part A		%
§ 270.14(b)(1)		General facility description	Attachment A		%
§ 270.14(b)(2)	§ 264.13(a)	Chemical and physical analyses	Attachment B	%	
§ 270.14(b)(3)	§ 264.13(b)	Development and implementation of waste analysis plan	Attachment B	%	
	§ 264.13(c)	Off-site waste analysis requirements	Attachment B	%	
§ 270.14(b)(4)	§ 264.14(a-c)	Security procedures and equipment	Attachment C		%
§ 270.14(b)(5)	§ 264.15(a-d)	General inspection requirements	Attachment D		%
	§ 264.174	Container inspections	Attachment D		%
§ 270.23(a)(2)	§ 264.602	Miscellaneous units inspections	Attachment D		%
§ 270.14(b)(6)		Request for waiver from preparedness and prevention requirements of Part 264 Subpart C	NA		
§ 270.14(b)(7)	264 Subpart D	Contingency plan requirements	Attachment F		%
	§ 264.51	Contingency plan design and implementation	Attachment F		%
	§ 264.52 (a) & (c-f)	Contingency plan content	Attachment F		%
	§ 264.53	Contingency plan copies	Attachment F		%
	§ 264.54	Contingency plan amendment	Attachment F		%
	§ 264.55	Emergency coordinator	Attachment F		%
	§ 264.56	Emergency procedures	Attachment F		%
§ 270.14(b)(8)		Description of procedures, structures or equipment for:	Attachment E		%
§ 270.14(b)(8)(i)		Prevention of hazards in unloading operations (e.g., ramps and special forklifts)	Attachment E		%
§ 270.14(b)(8)(ii)		Runoff or flood prevention (e.g., berms, trenches, and dikes)	Attachment E		%
§ 270.14(b)(8)(iii)		Prevention of contamination of water supplies	Attachment E		%
§ 270.14(b)(8)(iv)		Mitigation of effects of equipment failure and power outages	Attachment E		%
§ 270.14(b)(8)(v)		Prevention of undue exposure of personnel (e.g., personal protective equipment)	Attachment E		%
§ 270.14(b)(8)(vi) § 270.23(a)(2)	§ 264.601	Prevention of releases to the atmosphere	Module II Module IV Attachment M2 Attachment N		%

Regulatory Citation(s) 20.4.1.900 NMAC (incorporating 40 CFR 270)	Regulatory Citation(s) 20.4.1.500 NMAC (incorporating 40 CFR 264)	Description of Requirement	Added or Clarified Information		
			Section of the HWFP or Permit Application	Yes	No
	264 Subpart C	Preparedness and Prevention	Attachment E		%
	§ 264.31	Design and operation of facility	Attachment E		%
	§ 264.32	Required equipment	Attachment E Attachment F		%
	§ 264.33	Testing and maintenance of equipment	Attachment D		%
	§ 264.34	Access to communication/alarm system	Attachment E		%
	§ 264.35	Required aisle space	Attachment E		%
	§ 264.37	Arrangements with local authorities	Attachment F		%
§ 270.14(b)(9)	§ 264.17(a-c)	Prevention of accidental ignition or reaction of ignitable, reactive, or incompatible wastes	Attachment E		%
§ 270.14(b)(10)		Traffic pattern, volume, and controls, for example: Identification of turn lanes Identification of traffic/stacking lanes, if appropriate Description of access road surface Description of access road load-bearing capacity Identification of traffic controls	Attachment G		%
§ 270.14(b)(11)(i) and (ii)	§ 264.18(a)	Seismic standard applicability and requirements	Part B, Rev. 6 Chapter B		%
§ 270.14(b)(11)(iii-v)	§ 264.18(b)	100-year floodplain standard	Part B, Rev. 6 Chapter B		%
	§ 264.18(c)	Other location standards	Part B, Rev. 6 Chapter B		%
§ 270.14(b)(12)	§ 264.16(a-e)	Personnel training program	Attachment H		%
§ 270.14(b)(13)	264 Subpart G	Closure and post-closure plans	Attachment I & J		%
§ 270.14(b)(13)	§ 264.111	Closure performance standard	Attachment I		%
§ 270.14(b)(13)	§ 264.112(a)(b)	Written content of closure plan	Attachment I		%
§ 270.14(b)(13)	§ 264.112(c)	Amendment of closure plan	Attachment I		%
§ 270.14(b)(13)	§ 264.112(d)	Notification of partial and final closure	Attachment I		%
§ 270.14(b)(13)	§ 264.112(e)	Removal of wastes and decontamination/dismantling of equipment	Attachment I		%
§ 270.14(b)(13)	§ 264.113	Time allowed for closure	Attachment I		%
§ 270.14(b)(13)	§ 264.114	Disposal/decontamination	Attachment I		%
§ 270.14(b)(13)	§ 264.115	Certification of closure	Attachment I		%
§ 270.14(b)(13)	§ 264.116	Survey plat	Attachment I		%
§ 270.14(b)(13)	§ 264.117	Post-closure care and use of property	Attachment J		%
§ 270.14(b)(13)	§ 264.118	Post-closure plan; amendment of plan	Attachment J		%



Regulatory Citation(s) 20.4.1.900 NMAC (incorporating 40 CFR 270)	Regulatory Citation(s) 20.4.1.500 NMAC (incorporating 40 CFR 264)	Description of Requirement	Added or Clarified Information		
			Section of the HWFP or Permit Application	Yes	No
§ 270.14(b)(13)	§ 264.178	Closure/ containers	Attachment I		%
§ 270.14(b)(13)	§ 264.601	Environmental performance standards- Miscellaneous units	Attachment I		%
§ 270.14(b)(13)	§ 264.603	Post-closure care	Attachment I		%
§ 270.14(b)(14)	§ 264.119	Post-closure notices	Attachment J		%
§ 270.14(b)(15)	§ 264.142	Closure cost estimate	NA		%
	§ 264.143	Financial assurance	NA		%
§ 270.14(b)(16)	§ 264.144	Post-closure cost estimate	NA		%
	§ 264.145	Post-closure care financial assurance	NA		%
§ 270.14(b)(17)	§ 264.147	Liability insurance	NA		%
270.14(b)(18)	§ 264.149-150	Proof of financial coverage	NA		%
§ 270.14(b)(19)(i), (vi), (vii), and (x)		Topographic map requirements Map scale and date Map orientation Legal boundaries Buildings Treatment, storage, and disposal operations Run-on/run-off control systems Fire control facilities	Attachment O Part A Part B, Rev. 6 Chapter B, E		%
§ 270.14(b)(19)(ii)	§ 264.18(b)	100-year floodplain	Attachment O Part A Part B, Rev. 6 Chapter B, E		%
§ 270.14(b)(19)(iii)		Surface waters	Attachment O Part A Part B, Rev. 6 Chapter B, E		%
§ 270.14(b)(19)(iv)		Surrounding Land use	Attachment O Part A Part B, Rev. 6 Chapter B, E		%
§ 270.14(b)(19)(v)		Wind rose	Attachment O Part A Part B, Rev. 6 Chapter B, E		%
§ 270.14(b)(19)(viii)	§ 264.14(b)	Access controls	Attachment O Part A Part B, Rev. 6 Chapter B, E, F		%
§ 270.14(b)(19)(ix)		Injection and withdrawal wells	Attachment O Part A Part B, Rev. 6 Chapter B, E, F		%
§ 270.14(b)(19)(xi)		Drainage on flood control barriers	Part B, Rev. 6 Chapter B, E, F		%
§ 270.14(b)(19)(xii)		Location of operational units	Part B, Rev. 6 Chapter B		%

Regulatory Citation(s) 20.4.1.900 NMAC (incorporating 40 CFR 270)	Regulatory Citation(s) 20.4.1.500 NMAC (incorporating 40 CFR 264)	Description of Requirement	Added or Clarified Information		
			Section of the HWFP or Permit Application	Yes	No
§ 270.14(b)(20)		Other federal laws Wild and Scenic Rivers Act National Historic Preservation Act Endangered Species Act Coastal Zone Management Act Fish and Wildlife Coordination Act Executive Orders	Part B, Rev. 6 Chapter K		%
§ 270.15	§ 264 Subpart I	Containers	Attachment M1		%
	§ 264.171	Condition of containers	Attachment M1		%
	§ 264.172	Compatibility of waste with containers	Attachment M1		%
	§ 264.173	Management of containers	Attachment M1		%
	§ 264.174	Inspections	Attachment D Attachment M1		%
§ 270.15(a)	§ 264.175	Containment systems	Attachment M1		%
§ 270.15(c)	§ 264.176	Special requirements for ignitable or reactive waste	Attachment E Permit Module II		%
§ 270.15(d)	§ 264.177	Special requirements for incompatible wastes	Attachment E Permit Module II		%
	§ 264.178	Closure	Attachment I		%
§ 270.15(e)	§ 264.179	Air emission standards	Attachment E Attachment N		%
§ 270.23	264 Subpart X	Miscellaneous units	Attachment M2		%
§ 270.23(a)(1)	§ 264.601	Detailed unit description	Attachment M2		%
§ 270.23(a)(2)	§ 264.601	Prevention of releases to the atmosphere	Permit Module II Permit Module IV Attachment M2 Attachment N		%
§ 270.23(a)(2)	§ 264.602	Monitoring, analysis, inspection, response, reporting, and corrective action	Permit Module IV Attachment D Attachment M2 Attachment N		%
§ 270.23(a)(3)	§ 264.603	Post-closure care	Attachment J Attachment J1		%
§ 270.23(b)	§ 264.601	Hydrologic, geologic, and meteorologic assessments	Permit Module IV Attachment M2		%
§ 270.23(c)	§ 264.601	Potential exposure pathways	Permit Module IV Attachment M2 Attachment N		%
§ 270.23(d)		Demonstration of treatment effectiveness	Permit Module IV Attachment M2 Attachment N		%
	264 Subpart E	Manifest system, record keeping, and reporting	Permit Module I Permit Module II Permit Module IV Attachment B		%

**ATTACHMENT A**  
**Proposed Modified Permit Text**

**Table 1. Class 2 Hazardous Waste Facility Permit Modification Request**

<b>No.</b>	<b>Affected Permit Section</b>	<b>Item</b>	<b>Category</b>	<b>Attachment 1 Page #</b>
1	a.1. B-3a(1) b.1. B2-3 c.1. B3-1 c.2. B3-5 c.2. B3-10 c.3. B3-12b(3) d.1. Table B6-1 d.2. Table B6-2 d.3. Table B6-4 d.4. Table B6-4	Using Composite Headspace Gas Data and Compositing up to 20 Samples	B.1.d	A-3
2	a.1. B-3d(2) b.1. Table B6-1	Establishing Safety Conditions for Visual Examination (VE) of Waste Containers	B.2.b	A-19
3	a.1. TOC a.2. B1-1a(1) a.3. B1-1a(2) a.4. B1-1a(3)(ii) a.5. B1-1a(3)(iii) a.6. B1-1c(5) b.1. Table B6-4 b.2. Table B6-5 b.3. Table B6-5	Taking Samples of Headspace Gas through Existing Filter Vent Holes	B.1.d	A-24

## Item 1

### Using Composite Headspace Gas Data and Compositing up to 20 Samples

#### Description:

This PMR item proposes to clarify the conditions under which headspace gas samples may be composited in the laboratory. It also proposes to delineate the effects of compositing on the upper 90% confidence values ( $UCL_{90}$ ), which are the values used for regulatory decision making. In addition, this PMR item proposes specific reporting criteria for tentatively identified compounds (TICs) to ensure an equivalent level of reporting accuracy for composited and uncomposited headspace gas samples.

#### Basis:

Tables B-1 and B-3 of the WIPP Permit require that laboratories analyzing headspace gas samples use Environmental Protection Agency (EPA)-specified analytical methods Modified TO-14 or modified Method 8240/8260. Method 8260 is an SW-846 method for performing volatile organic compound analysis on samples. SW-846 Method 8260 is an aqueous method, so the permit requires that a modified Method 8260 be used to account for the analysis of gas samples. Therefore, the discussion of compositing aqueous samples in Section 7.5.7 of SW-846 Method 8260 is applicable to gas samples (A copy of Method 8260 is included in Attachment B). However, the permit does not indicate how the results of the composited data should be applied or how the current data reporting and validation requirements apply to composited results.

This PMR item provides clarification for using headspace gas data generated using the modified Method 8260 compositing procedure. This PMR item provides additional requirements for the use of composited headspace gas data to satisfy permit requirements.

This PMR item also changes the permit to assure that the mean concentration of tentatively identified compounds (TICs) and the calculated  $UCL_{90}$  are not adversely affected by the compositing of headspace gas samples.

Data were collected at the Idaho National Engineering and Environmental Laboratory (INEEL) and the Rocky Flats Environmental Technology Site (RFETS) from both mixed and non-mixed waste streams respectively. These waste streams had undergone headspace gas sampling and analysis both with and without sample compositing.

The data were subjected to robust statistical analyses and the results indicate that there are no statistically significant differences in the headspace gas data for the 28 target analytes required by the HWFP. The data also show that  $UCL_{90}$  values for composite samples are consistently equivalent to or greater than  $UCL_{90}$  values for individual samples and thus are conservative. The graphical displays of those data and the technical paper for that study are included in Attachment B.

This PMR item establishes requirements that ensure data usability and protect human health and the environment.

## Discussion:

Permit Section B-3a(1) requires that:

*"Every TRU mixed waste container will be sampled and analyzed to determine the concentrations of VOCs (presented in Table B-3) in headspace gases."*

There are two aspects of this compositing request that are of importance to satisfying this permit requirement. One is a demonstration that composited values adequately represent the concentration of VOCs in containers of TRU mixed waste and that decision-making using the UCL<sub>90</sub> value is conservative.

The second area of importance is TICs. The following discussion demonstrates that this PMR item assures that TICs are identified and reported in a consistent manner.

### Composited Values

Table B-3 in the HWFP specifies the analytes and methods required for headspace gas sample analysis. One of the allowable methods specified in Table B-3 is a modified Method 8260. SW-846 Method 8260 establishes the analytical protocols for determining volatile organic compound (VOC) concentrations in aqueous samples. One of the protocols specified in SW-846 Method 8260 is for compositing samples in the laboratory. Section 7.5.7 describes the procedure for compositing samples prior to gas chromatography/mass spectrometry (GC/MS) analysis. The method allows for up to 5 aqueous samples to be composited and requires that equal volumes of each sample be composited into a glass syringe prior to introducing the sample into the analytical equipment. Because SW-846 Method 8260 is a method for aqueous samples, the permit requires that a modified Method 8260 be used to account for analysis of gas samples.

The EPA SW-846, Methods Information Communication Exchange (MICE) Service was contacted by e-mail with a specific request to describe the origin of the 5-sample composite procedure described in SW-846 Method 8260 regarding the number of samples in the composite. The following response was received (A printed copy of the e-mail is provided in Attachment B):

*"The use of 5 samples for compositing is mostly based on the largest syringe size appropriate for this analysis, 25-ml. For compositing you need equal volumes of each of the samples; hence, the recommendation to take a 5-ml aliquot from 5 different samples. As stated in the method, you may use a smaller number of samples, provided that equal volumes of each sample are composited, or you may use a proportionately smaller syringe.*

*As for using more than 5 samples, there is nothing in the method that says you can't do it.*

*However, as volumes get smaller the associated error becomes larger. So, you will need to take precautions to minimize the errors associated with the measurement of smaller volumes. If you use a larger syringe to accommodate more than 5 samples, you need to determine what volume of aliquot to withdraw from the composite sample that will be representative of that sample."*

This response indicates that, provided the error associated with measuring smaller volumes is minimized, more than 5 samples can be composited. In the case of the modified Method 8260 that is required by the HWFP, the modifications to the method for the

analysis of gas samples involves using a 250 ml SUMMA® canister instead of a 25 ml syringe for holding the composited sample and delivering it to the analytical instrument.

Using a 25 ml syringe and a 5 composite sample results in a 5 ml aliquot from the 5 individual samples being placed in the syringe for the aqueous samples following SW-846 Method 8260. Using a 5 ml volume ensures that any sampling error associated with collecting the aliquot from the individual containers is small. Using the same volume from each of the individual samples (i.e., the 5 ml) ensures representativeness for the composite sample that is analyzed.

In the case of the modified Method 8260, using a 250 ml SUMMA® canister and a 20 composite sample results in a 12.5 ml aliquot from 20 individual containers being placed in the SUMMA® canister for the gas samples. The accuracy and precision of the composited sample results relative to individual container sample results using the modified Method 8260 was corroborated using data from actual waste streams. This was done by evaluating the mean concentrations from data collected using composite samples and the mean concentrations from data collected using individual container samples. The *Technical Evaluation of Headspace Gas Compositing*, attached included in Attachment B, contains the results of this evaluation and shows that the mean concentrations are equivalent at a 90% confidence level on the mean for up to 20 to 1 composite samples. Therefore, the error associated with the 12.5 ml aliquot sampling does not result in less precise measurements for up to 20 to 1 compositing. Using the same volume from each of the individual samples (i.e., the 12.5 ml) once again ensures representativeness for the composite sample that is analyzed. Therefore, the modified Method 8260 that addresses the analysis of gas samples allows the compositing of up to 20 samples, while ensuring that the errors are minimized and representativeness is maintained.

Therefore, the Permittees believe that the compositing methodology provided in Section 7.5.7 of SW-846 Method 8260 is allowable as long as laboratory-specific procedures ensure that the method is modified appropriately to maintain sample integrity for composite gas samples. Analyses included in the technical paper in Attachment B show that sample composites of up to 20 to 1 are reasonable. A composite of up to 20 to 1 is set in this PMR item as a practical limit for several reasons. First, sampling batches are limited by the HWFP to 20 samples, plus sample batch quality control samples. Second, the availability of airtight syringes for removing the samples from the individual SUMMA® canister for compositing into the composite SUMMA® canister limits composite samples to 12.5 ml or larger.

Worker and public health is ensured by entering individual container headspace gas concentrations into the WIPP Waste Information System (WWIS) and averaging them to compare to the limits established in Module IV. A second level of assurance is maintained by conducting VOC monitoring in accordance with Permit Attachment N. In order to ensure that the data usability is maintained, this PMR item requires that the composite sample results be assigned to each container used in the composite sample and subsequently entered into the WWIS. In addition, the requirement to assign the results of the composite

sample to each of the containers that made up that sample is applicable to reporting any TICs associated with the analytical results. The analyses in the technical paper in Attachment B demonstrate that TICs in concentrations that exceed the immediately dangerous to life and health (IDLH) levels would be detected in composite samples.

Confirmation and assignment of hazardous waste codes is performed on a waste stream basis. Section B4-3d specifies the requirements for confirming hazardous waste codes using headspace gas data as follows:

*“The Permittees shall require sites to use acceptable knowledge to identify spent solvents associated with each TRU mixed waste stream or waste stream lot. Headspace-gas data will then be used to confirm acceptable knowledge concerning the presence or absence of F-listed solvents and concentration of applicable toxicity characteristic solvents. Sites shall confirm the assignment of F-listed hazardous waste codes (20 NMAC 4.1.200, incorporating 40 CFR § 261.31) by evaluating the average concentrations of each VOC detected in container headspace gas for each waste stream or waste stream lot using the upper 90 percent confidence limit (**UCL<sub>90</sub>**). The **UCL<sub>90</sub>** for the mean concentration shall be compared to the program required quantitation limit (**PRQL**) for the constituent. If the **UCL<sub>90</sub>** for the mean concentration exceeds the **PRQL**, sites shall reevaluate their acceptable knowledge information and determine the potential source of the constituent.”*

The **UCL<sub>90</sub>** value for the mean concentration is calculated from the headspace gas results following the methodology specified in Section B2-3. Because the **UCL<sub>90</sub>** is based on the average value across the waste stream, the use of composited headspace gas sample data is equivalent to individual container headspace gas data as long as the containers that are being composited are from the same waste stream. An analysis was conducted that demonstrates that the use of compositing results in calculating the **UCL<sub>90</sub>** result in a value that is equivalent to or more conservative than the **UCL<sub>90</sub>** that would have been calculated from individual drum results. The technical paper describing this analysis is in Attachment B.

All quality assurance/quality control (QA/QC) and TIC requirements associated with the sampling procedure and the analysis method (e.g., field duplicates, laboratory control samples, etc.) used must be conducted in accordance with the requirements of the permit. Section 3.2 of the technical paper in Attachment B documents that the TIC description criteria in Permit Attachment B3-1 are valid for samples that are composited up to 20 to 1 as proposed in this PMR item.

#### Reporting Tentatively Identified Compounds

In order to facilitate implementation of the HWFP with regard to TIC identification and reporting, the CBFO issued Clarification CAO-00-065 in June 2000. This clarification provides an interpretation for how to account for instrument noise when using automated software to evaluate the results of GC/MS methods for TICs. This interpretation provides direction for identifying TICs by using a limit of 10% of the nearest internal standard. This



clarification states:

*Automated software can be used to assist in the determination of TICs. Specifically, software can be set to limit TIC identification to account for instrument noise. This can be done by setting the software to perform a forward search of the NIST library of mass spectra for tentatively identified compounds for all chromatographic peaks greater than 10 percent of the nearest internal standard.*

The 10% of the nearest internal standard criterion is based on the requirements for the Superfund Contract Laboratory Program, Exhibit D - Volatiles, Section 11.1.2.2. The criteria for how well the TIC must match the reference spectra from the compound library is presented in HWFP, Attachment B3, Section B3-1 as follows:

- *Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.*
- *The relative intensities of the major ions should agree within  $\pm 20$  percent.*
- *Molecular ions present in the reference spectrum should be present in the sample spectrum.*
- *Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.*
- *Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks.*
- *TICs for headspace gas analyses that are performed through FTIR analyses shall be identified in accordance with the specifications of SW-846 Method 8410.*

The first 5 criteria are direct quotes for GC/MS methods from SW-846, Method 8260B, Section 7.6.2 and the Superfund Contract Laboratory Program, Exhibit D - Volatiles, Section 11.1.2.4. The sixth criteria is specific to the use of a non-GC/MS method (i.e., FTIR) for performing laboratory analysis.

Clarification CAO-00-065, Revision 2 also provides an interpretation for reporting TICs that is based on compounds present in the 20.4.1.200 NMAC (incorporating 40 CFR § 261) Appendix VIII. The clarification states:

*Only those compounds that are listed as hazardous constituents in 40 CFR 261, Appendix VIII need to be included in the reference library. This library can be further reduced to include those compounds being sought by the analysis. This applies to totals analysis and headspace gas analysis. For example, headspace gas analysis need only use a subset of Appendix VIII that includes VOCs.*

The approach for identifying and reporting TICs presented in this clarification (i.e., the 10% of the nearest internal standard and Appendix VIII VOCs) has been implemented as part of

the waste characterization program for the certified sites. These sites have been audited by the Permittees and the audit reports have been approved by the NMED.

The language proposed as part this PMR item incorporates language that renders Clarification CAO-00-065 unnecessary. To address the use of the 20.4.1.200 NMAC (incorporating 40 CFR § 261) Appendix VIII list, this PMR item requires only those TICs that appear in the 20.4.1.200 NMAC (incorporating 40 CFR § 261) Appendix VIII list to be identified and reported during the chemical analysis.

To account for instrument noise when using automated software, this PMR item incorporates reporting level requirements for TICs. To ensure that TICs in composited samples are reported at a level that is consistent with what is currently required by the HWFP and approved during the audits, the proposed reporting levels are related to the nearest internal standard and are dependent on the number of samples being composited. The automated software in use at generator/storage sites was evaluated to ensure that the reporting levels proposed below are achievable. The software allows a minimum value of 0.1% to be entered for the area of the TIC relative to the nearest internal standard. The minimum value proposed for any reporting level is 0.5%; therefore, all of the proposed reporting levels are achievable. There are four TIC reporting levels that are being proposed as part of this PMR:

TIC Reporting Level 1: Individual container samples - This PMR item proposes language that states that the TICs reported must have a response that is a minimum of 10% of the area of the nearest internal standard for individual container samples.

TIC Reporting Level 2: Compositing 2 to 5 samples - This PMR item proposes language that modifies the 10% of the nearest internal standard criterion to account for the potential dilution due to compositing 2 to 5 individual container samples. The most conservative case is for only 1 of the 5 samples to contain the TIC resulting in a maximum potential dilution of 5 times the dilution from TIC Reporting Level 1. To account for this potential dilution, TIC Reporting Level 2 requires that TICs reported must have a response that is a minimum of 2% of the area of the nearest internal standard (i.e., one fifth of TIC Reporting Level 1). This minimum percentage provides an equivalent reporting level for the most conservative case. If the TIC is present in more than one of the samples, TIC Reporting Level 2 is even more conservative.

TIC Reporting Level 3: Compositing 6 to 10 samples - This PMR item proposes language that modifies the 10% of the nearest internal standard criterion from to account for the potential dilution due to compositing 6 to 10 individual container samples. The most conservative case is for only 1 of the 10 samples to contain the TIC resulting in a maximum potential dilution of 10 times the dilution from TIC Reporting Level 1. To account for this potential dilution, TIC Reporting Level 3 requires that TICs reported must have a response that is a minimum of 1% of the area of the nearest internal standard (i.e., one tenth of TIC Reporting Level 1). This minimum percentage provides an equivalent reporting level for the most conservative case. If

the TIC is present in more than one of the samples, TIC Reporting Level 3 is even more conservative.

TIC Reporting Level 4: Compositing 11 to 20 samples - This PMR item proposes language that modifies the 10% of the nearest internal standard criterion to account for the potential dilution due to compositing 11 to 20 individual container samples. The most conservative case is for only 1 of the 20 samples to contain the TIC resulting in a maximum potential dilution of 20 times the dilution from TIC Reporting Level 1. To account for this potential dilution, TIC Reporting Level 4 requires that TICs reported must have a response that is a minimum of 0.5% of the area of the nearest internal standard (i.e., one twentieth of TIC Reporting Level 1). This minimum percentage provides an equivalent reporting level for the most conservative case. If the TIC is present in more than one of the samples, TIC Reporting Level 4 is even more conservative.

### **Proposed Revised Permit Text:**

#### **a. 1. Section B-3a(1)**

Every TRU mixed waste container or statistically selected containers from waste streams that meet the conditions for reduced headspace gas sampling listed in this section will be sampled and analyzed to determine the concentrations of VOCs (presented in Table B-3) in headspace gases. If composite samples are used, containers used in the composite sample must be from the same waste stream with no more than 20 containers being included in a single composite sample. Sampling protocols, equipment, and QA/QC methods for headspace-gas sampling are provided in Permit Attachment B1. In accordance with EPA convention, identification of hazardous constituents detected by gas chromatography/mass spectrometry methods that are not on the list of target analytes shall be reported. These compounds are reported as tentatively identified compounds (**TICs**) in the analytical batch data report and shall be added to the target analyte list if detected in a given waste stream, if they appear in the 20 NMAC 4.1.200 (incorporating 40 CFR § 261) Appendix VIII, and if they are detected in 25% of the samples from a given waste stream. The headspace gas analysis method Quality Assurance Objectives (**QAOs**) are specified in Permit Attachment B3.

#### **b.1. Section B2-3**

Once sufficient sampling and analysis has occurred, the waste characterization will proceed.

The assessment will be made with 90 percent confidence. The  $UCL_{90}$  for the mean concentration of each contaminant will be calculated in accordance with the following equation:

$$UCL_{90} = \bar{x} + \frac{t_{\alpha, n-1} S}{\sqrt{n}} \quad (B2-10)$$

When composite headspace gas sample results are used, the mean, standard deviation and t-statistic are based on the number of composite samples analyzed, rather than the number of drums sampled. If the  $UCL_{90}$  for the mean concentration is less than the regulatory threshold limit, the waste stream will not be assigned the hazardous waste code for this contaminant. If the  $UCL_{90}$  is greater than or equal to the regulatory threshold limit, the waste stream will be assigned the hazardous waste code for this contaminant.

#### c.1. Section B3-1

##### Identification of Tentatively Identified Compounds

In accordance with SW-846 convention, identification of compounds detected by gas chromatography/mass spectrometry methods that are not on the list of target analytes shall be reported. Both composited and individual container hHeadspace gas, volatile analysis (TCLP/Totals), and semi-volatile (TCLP/Totals) shall be subject to tentatively identified compound (**TIC**) reporting. These TICs for GC/MS Methods are identified in accordance with the following SW-846 criteria:

- ! Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- ! The relative intensities of the major ions should agree within  $\pm 20$  percent.
- ! Molecular ions present in the reference spectrum should be present in the sample spectrum.

- ! Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- ! Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks.

! The reference spectra used for identifying TICs shall include, at minimum, all of the available spectra for compounds that appear in the 20.4.1.200 NMAC (incorporating 40 CFR Part 261) Appendix VIII list. The reference spectra may be limited to VOCs when analyzing headspace gas samples.

- ! TICs for headspace gas analyses that are performed through FTIR analyses shall be identified in accordance with the specifications of SW-846 Method 8410.

TICs shall be reported as part of the analytical batch data reports for GC/MS Methods in accordance with the following minimum criteria:

! a TIC in an individual container headspace gas or solids sample shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 10% of the area of the nearest internal standard.

! a TIC in a composited headspace gas sample that contains 2 to 5 individual container samples shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 2% of the area of the nearest internal standard.

! a TIC in a composited headspace gas sample that contains 6 to 10 individual container samples shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 1% of the area of the nearest internal standard.

! a TIC in a composited headspace gas sample that contains 11 to 20 individual container samples shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 0.5% of the area of the nearest internal standard.

TICs that meet the SW-846 identification criteria, are detected in 25 percent of all samples from a given waste stream, and that appear in the 20.4.1.200 NMAC (incorporating 40 CFR § 261) Appendix VIII list, will be compared to acceptable knowledge data to determine if the TIC is a listed waste in the waste stream. TICs identified through headspace gas analyses that meet the Appendix VIII list criteria and the 25 percent identification criteria for a waste stream will be added to the headspace gas waste stream target list regardless of the hazardous waste listing associated with the waste stream. TICs reported from the Totals VOC or SVOC analyses may be excluded from the target analyte list for a waste stream if the TIC is a constituent in an F-listed waste whose presence is attributable to waste packaging materials or radiolytic degradation from acceptable knowledge documentation. If a listed waste constituent TIC cannot be attributed to waste packaging materials, radiolysis, or other origins, the constituent will be added to the target analyte list and new hazardous waste codes will be assigned, if appropriate. TICs subject to inclusion on the target analyte list that are toxicity characteristic parameters shall be added to the target analyte list regardless of origin because the hazardous waste designation for these codes is not based on source. However, for toxicity characteristic and non-toxic F003 constituents, the site may take concentration into account when assessing whether to add a hazardous waste code. If a target analyte list for a waste stream is expanded due to the presence of TICs, all samples collected from that waste stream will be analyzed for constituents on the expanded list.

#### c. 2. Section B3-5

##### Completeness

Laboratory completeness shall be expressed as the number of samples analyzed with valid results as a percent of the total number of samples submitted for analysis. A composited sample is treated as one sample for the purposes of completeness, because only one sample is run through the analytical instrument. Valid results are defined as results that meet the data usability criteria based on application of the Quality Control Criteria specified in Tables B3-2 and B3-3; and meet the detection limit, calibration representativeness, and comparability criteria within this section. The Permittees shall require that participating laboratories meet the

completeness criteria specified in Table B3-2.

c. 3. Section B3-10

An Analytical Batch Data Report or equivalent includes analytical and on-line data from the sampling and analysis of TRU-mixed waste for an analytical batch of up to 20 samples.

Analytical Batch Data Reports or equivalent that contain results for composited headspace gas samples must contain sufficient information to identify the containers that were composited for each composite sample. Because Analytical Batch Data Reports are generated based on the number of samples analyzed, an Analytical Batch Data Report may contain results that are applicable to more than 20 containers depending on how many composite samples are part of the report, but may not exceed a total of 20 samples analyzed. Totals/TCLP analyses results and headspace gas sampling and analyses results are in the Analytical Batch Data Reports, which may also include summarized sample results, summarized QA sample results and recoveries, raw data, dates and times of analysis of all samples, and a case narrative describing any problems encountered or deviations from the approved analytical methods that occurred during the preparation and analysis of all samples.

c. 4. Section B3-12b(3)

**B3-12b(3) WIPP Waste Information System (WWIS) Data Reporting**

The WWIS Data Dictionary includes all of the data fields, the field format and the limits associated with the data as established by this WAP. These data will be subjected to edit and limit checks that are performed automatically by the database, as defined in the WIPP Waste Information System User's Manual for Use by Shippers/Generators (DOE-1997). If a container was part of a composite headspace gas sample, the analytical results from the composite sample must be assigned as the container headspace gas data results, including associated TICs.

d. 1. Table B6-1

<u>51a</u>	<u>Are procedures in place to ensure that if a container was part of a composite headspace gas sample, the analytical results from the composite sample are assigned as the container headspace gas data results in the WWIS.</u> <u>B3-12b(3)</u>
------------	---



d. 2. Table B6-2

126a	<p>Are procedures documented to ensure that the following criteria are met with regard to the recognition and reporting of TICS for GC/MS Methods for homogeneous solids and soils and gravels:</p>
!	<p>Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.</p>
!	<p>The relative intensities of the major ions should agree within <math>\pm 20</math> percent.</p>
!	<p>Molecular ions present in the reference spectrum should be present in the sample spectrum.</p>
!	<p>Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.</p>
!	<p>Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks.</p>
!	<p>The reference spectra used for identifying TICS shall include, at minimum, all of the available spectra for compounds that appear in the 20.4.1.200 NMAC (incorporating 40 CFR Part 261) Appendix VIII list. The reference spectra may be limited to VOCs when analyzing headspace gas samples.</p>
!	<p>TICs for headspace gas analyses that are performed through FTIR analyses shall be identified in accordance with the specifications of SW-846 Method 8410.</p>
	<p>TICs shall be reported as part of the analytical batch data reports for GC/MS Methods in accordance with the following minimum criteria:</p>
!	<p>a TIC in an individual container headspace gas or solids sample shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 10% of the area of the nearest internal standard.</p>
	<p>(Section B3-1)</p>

d.3. Table B6-4

220	<p>Are procedures in place to ensure that all VOC analyses are evaluated using the following criteria:</p> <ul style="list-style-type: none"> <li>C Precision is assessed through evaluation of laboratory duplicates, Laboratory Control Sample (LCS) replicates, and PDP blind audit samples in comparison to Table B3-3</li> <li>C Accuracy is assessed through evaluation of LCS samples and blind PDP audit samples in comparison to criteria in Table B3-3</li> <li>C MDL's are expressed in nanogram/liter</li> <li>C Laboratory completeness shall be expressed as the number of samples analyzed with valid results as a percent of the total number of samples collected. <u>A composited sample is treated as one sample for the purposes of completeness, because only one sample is run through the analytical instrument</u></li> <li>C Comparability shall be achieved through the use of standardized methods, through the consistent application of data usability criteria, and traceable standards and through successful participation in the PDP program</li> <li>C Representativeness will be achieved through the use of standardized sample collection methods with a demonstrated absence of blank contamination</li> <li>C All method detection limits and program required detection limits shall be less than the Program Required Detection Limits listed in Table B3-2 and the detection limit study procedures shall be documented in laboratory SOPs. In addition, the laboratory shall demonstrate that they are capable of meeting the Program Required Detection Limits by analyzing at least one calibration standard below the PRQL</li> </ul> <p>(Section B3-5)</p>
-----	---

d.4. Table B6-4

222a

Are procedures documented to ensure that the following criteria are met with regard to the recognition and reporting of TICs for GC/MS Methods for headspace gas sampling:

- ! Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- ! The relative intensities of the major ions should agree within  $\pm 20$  percent.
- ! Molecular ions present in the reference spectrum should be present in the sample spectrum.
- ! Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- ! Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks.
- ! The reference spectra used for identifying TICs shall include, at minimum, all of the available spectra for compounds that appear in the 20.4.1.200 NMAC (incorporating 40 CFR Part 261) Appendix VIII list. The reference spectra may be limited to VOCs when analyzing headspace gas samples.
- ! TICs for headspace gas analyses that are performed through FTIR analyses shall be identified in accordance with the specifications of SW-846 Method 8410.

(Section B3-1)

222b

Are procedures in place to assure that TICs are reported as part of the analytical batch data reports for GC/MS Methods in accordance with the following minimum criteria:

- ! a TIC in an individual container headspace gas or solids sample shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 10% of the area of the nearest internal standard.
- ! a TIC in a composited headspace gas sample that contains 2 to 5 individual container samples shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 2% of the area of the nearest internal standard.
- ! a TIC in a composited headspace gas sample that contains 6 to 10 individual container samples shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 1% of the area of the nearest internal standard.
- ! a TIC in a composited headspace gas sample that contains 11 to 20 individual container samples shall be reported in the analytical batch data report if the TIC meets the SW-846 identification criteria listed above and is present with a minimum of 0.5% of the area of the nearest internal standard.

(Section B3-1)

## **Item 2**

### **Establishing Safety Conditions for Visual Examination (VE) of Waste Containers**

#### **Description:**

This PMR item proposes to establish safety conditions for selecting containers that are visually examined as a QC check on radiography.

#### **Basis:**

Permit Attachment B1, Section B1-3b(3), recognizes that there are some conditions that could prove hazardous to personnel performing visual examination (VE); therefore, this permit section establishes a provision for providing VE personnel with radiography results if “items or conditions” exist that “could pose a hazard to VE personnel.” Permit Attachment B, Section B-3d(2) provides additional flexibility to minimize VE personnel exposure by allowing the VE to take place during coring operations.

This PMR item expands on these provisions by allowing sites performing VE to establish container safety criteria for selecting containers that will be opened for VE as a QC check on radiography based on information about the waste and the VE operations at the generator site.

The container safety conditions will establish the worker safety criteria that a container must meet prior to being selected for VE as a QC check on radiography. If a randomly selected container does not meet the container safety conditions, another container must be randomly selected from the same Summary Category Group because the originally selected container could pose a radiation hazard to VE personnel. However, the safety conditions must not reduce the number of containers that are visually examined as a QC check on radiography.

This PMR item incorporates EPA guidance for worker safety and protection of public health and the environment (Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste, 62 FR 62079, 11-20-97). This document is included as Attachment C. This PMR item applies to VE activities done as a QC check on radiography.

#### **Discussion:**

The WIPP HWFP requires that VE of transuranic (TRU) waste containers be conducted as a QC check on radiography. Containers are randomly selected for VE to determine, with acceptable confidence, what the miscertification rate for radiography is on a Summary Category Group basis.

Each site that performs radiography must have facilities for conducting VE of waste containers as a QC check on radiography. Each site operates within specific conditions that are related to the VE facility operational limitations, site-specific regulatory compliance requirements, and waste composition. The Joint NRC/EPA Guidance (62 FR 62079, 11-20-97) states that:

*“Flexibility in the Resource Conservation and Recovery Act (RCRA) requirements is emphasized so that the As Low As is Reasonably Achievable (ALARA) concept can be incorporated into the mixed waste testing activities. If other Atomic Energy Act (AEA) requirements, or RCRA requirements are difficult to meet in a specific mixed waste management situation, licensees should seek resolution by requesting license amendments, approval of modifications to their RCRA permits or interim status Part A applications, or resolution under both authorities.”*

Based on the NRC/EPA guidance, 10 CFR Part 835, and DOE Order 435.1, all mixed waste characterization activities should incorporate the ALARA concept. All of these documents are included as Attachment C. Because the VE operations addressed by this PMR item are conducted for QC purposes and not for initial data collection, minimizing worker exposure and ensuring safety by applying the ALARA concept for the VE process is totally compatible with the purposes of the WIPP Permit.

Also, sites will typically prohibit introduction into gloveboxes of certain items that might pose a threat to the integrity of the glovebox containment properties. For example, sharp items that could cut or puncture gloves are typically precluded to minimize radiological risk. Pursuant to Section 1006 of the Resource Conservation and Recovery Act, 42 U.S.C. §6905, establishing these safety conditions will avoid application of permit conditions in a manner that is inconsistent with the requirements of the Atomic Energy Act.

The permit currently contains several provisions for protecting VE personnel while performing VE on containers of TRU waste as a QC check on radiography. Section B1-3b(3) states:

*“Visual examination shall be performed on a statistically determined portion of waste containers to verify the results of radiography. With the exception of items or conditions that could pose a hazard to visual examination personnel, the radiography results shall not be made available until after the visual examination is completed.”*

This permit provision ensures VE personnel safety based on the results of radiography. For example, if a container appears to contain a radioactive source that may pose a hazard, that information may be provided to VE personnel to ensure safety.

Another permit provision increases worker safety by limiting exposure. This provision is in Permit Attachment B, Section B-3d(2):

*“For homogenous waste and soils/gravels selected for sampling, the containers opened for sampling may be used to help fulfill the visual examination requirements.”*

This section incorporates the ALARA concept by eliminating exposures due to handling and opening additional containers. This is accomplished by allowing containers that have already been randomly selected for solid sampling and analysis, moved to a glove box, and opened, to be visually examined at that time.

This PMR item ensures worker safety by incorporating the ALARA concept into the selection process for VE containers to be used as a QC check on radiography. This PMR item accomplishes this by allowing sites performing VE to establish safety conditions that must be met prior to opening a container during VE for the purpose of radiography QC. Specifically, this PMR item proposes that:

- A site may establish container (e. g., radiological) safety conditions that must be met prior to opening containers for VE as a QC check on radiography.
- All safety conditions must be based on characteristics of the waste and the site-specific operational safety requirements for VE (e.g., VE facility limitations and Hazards Analysis)
- The method for determining the container safety conditions, the analysis performed, and the actual conditions established must be part of the site's documentation that is submitted to the CBFO for approval (e. g., Quality Assurance Project Plan (QAPjP), Standard Operating Procedures (SOP)).
- If a randomly selected container does not meet the container safety conditions, another randomly selected container from the same Summary Category Group must be visually examined in its place.
- Container safety conditions that are established may not reduce the number of containers that are visually examined based on the statistical requirements of Permit Attachment B2.

An example of the need for these safety conditions had been documented at RFETS as indicated in the documentation included in Attachment C. This example includes finding crushed glass in the RFETS container.

## Proposed Revised Permit Text:

### a. 1. Section B-3d(2)

To confirm the results of radiography, a statistically selected number of the TRU mixed waste container population will be visually examined by opening containers to inspect waste contents to verify radiography results. Permit Attachment B2 contains the approach used to statistically select the number of drums to be visually examined. For homogenous waste and soils/gravels selected for sampling, the containers opened for sampling may be used to help fulfill the visual examination requirements. A site may establish container safety conditions that must be met prior to opening containers for VE as a QC check on radiography. The establishment and use of container safety conditions are subject to the following criteria:

- C All container safety conditions must be based on characteristics of the waste and the site-specific operational safety requirements for VE (e.g., VE facility limitations and Hazards Analysis, presence of excess broken glass in the container, high radioactivity)
- C The method for determining the container safety conditions, the analysis performed, and the actual conditions established must be part of the site's documentation that is submitted to the CBFO for approval (e. g., QAPjP, SOP) .
- C If a randomly selected container does not meet the container safety conditions, another randomly selected container from the same Summary Category Group must be visually examined in its place.
- C Container safety conditions that are established may not reduce the number of containers that are visually examined based on the statistical requirements of Permit Attachment B2.



b. 1. Table B6-1

28a	<p><u>If a site has established container safety conditions that must be met prior to opening containers for VE as a QC check on radiography is there documentation that the following criteria have been used:</u></p> <ul style="list-style-type: none"> <li><u>C</u> <u>All container safety conditions must be based on characteristics of the waste and the site-specific operational safety requirements for VE (e.g., VE facility limitations and Hazards Analysis, presence of excess broken glass in the container, high radioactivity)</u></li> <li><u>C</u> <u>The method for determining the container safety conditions, the analysis performed, and the actual conditions established must be part of the site's documentation that is submitted to the CBFO for approval (e. g., QAPjP, SOP) .</u></li> <li><u>C</u> <u>If a randomly selected container does not meet the container safety conditions, another randomly selected container from the same Summary Category Group must be visually examined in its place.</u></li> <li><u>C</u> <u>Container safety conditions that are established may not reduce the number of containers that are visually examined based on the statistical requirements of Permit Attachment B2.</u></li> </ul> <p><u>(Section B-3d(2))</u></p>
-----	--

### Item 3

## Taking Samples of Headspace Gas through Existing Filter Vent Holes

### Description:

This PMR item proposes to define requirements for headspace gas sampling through the existing filter vent hole.

### Basis:

Permit Attachment B1 provides methodologies for headspace gas sampling through the filter vent and through the drum lid. The methodology for sampling through the drum lid in Section B1-1a(3)(ii) only provides specific requirements for how the sampling should be conducted using the drum punch system; however, another method for sampling through the drum lid is to take a sample through an existing filter vent hole.

This PMR item provides an additional headspace gas sampling methodology for sampling through the drum lid and establishes equivalent requirements for performing the sampling through an existing filter vent hole. This approach also serves to reduce the creation of waste (e.g., punctured filters) and provides an alternative to punching drums that are already filtered.

### Discussion:

Permit section B1-1a(3)(ii) requires that:

*“Sampling through the drum lid may be performed as an alternative to sampling through the drum’s filter if an airtight seal can be maintained.”*

This statement correctly indicates that a valid sample can be taken through the drum lid instead of through the filter if an airtight seal can be maintained, which should apply equally to both a newly punctured hole or an existing filter vent hole in the drum lid. Therefore, if the filter is replaced with an airtight seal that can be used for sampling, it would meet the requirement that an airtight seal be maintained to obtain a representative sample. Replacing the filter with the airtight seal must be done as quickly as practicable to ensure that a representative sample can be taken. This PMR item also allows the use of a self-tapping screw for gaining access to the drum headspace gas instead of using a filter.

A study has been conducted at RFETS to ascertain the appropriate time limit between the removal of the filter vent and the insertion of an airtight seal on a pipe overpack container (POC) to ensure that the headspace gas sample is representative. The test plan and the final report are included as Attachment D. This study demonstrates that by immediately replacing the filter with the airtight seal, representative samples can be obtained. In the

RFETS study, the average time for replacing the filter with the airtight fitting was on the order of 33 seconds. The study, however, demonstrated that for cases approaching 5½ minutes, a representative sample can be obtained.

Implementing this methodology for sampling through an existing filter vent hole results in several benefits.

- The first benefit is that it provides an efficient method to sample POCs. Existing methods in the permit are not efficient. (Program officials at the RFETS have expressed concern that inserting the needle through the filter and the POC holes is not practical based on their judgement.)
- Another benefit is that it provides an opportunity for waste minimization by providing an alternative to destroying filters. Waste generators are required to certify that they have developed a waste minimization plan and operate their facility in compliance with that waste minimization plan. The ability to sample through the existing filter vent hole maximizes waste reduction at the generator/storage facilities that employ this technique. It is not necessary to destroy existing filters and thereby reduces waste generation. The disposal of filters not only creates additional waste it also adds to potential worker exposure through the need for waste characterization and subsequent waste handling operations. The filters cost approximately 35 to 75 dollars each and since the DOE has one budget for environmental management activities the money spent on replacing filters could be better directed towards closure of the generator/storage sites.
- Another benefit is reduced worker exposure. When sampling POCs it is impractical to sample through the existing filter vent hole. POCs have a one quarter inch steel plate with four 3/32 inch holes beneath the existing filter vent. Inserting a sampling needle through the plate is impossible using techniques authorized by the HWFP. Attempting to locate one of the four small holes by inserting a needle through a filter is difficult and causes undue and unnecessary worker exposure. A radiological assessment of exposure based on a time and motion study was performed for the Central Confirmation Facility Proposal. This study is included in Attachment D. Based on this study, the average time that an operator is expected to spend taking a headspace gas sample is on the order of 7 minutes. The time to use the airtight sample device is expected to be comparable. However, operators could spend significantly more time trying to insert a needle through the filter and one of the small holes in the POC as illustrated in the POC detail information in Attachment D. The method proposed in this PMR item allows the generator/storage site to keep sampling time to a minimum, thereby keeping minimizing doses to operators. This supports the DOE's mandate to maintain radiological doses as low as reasonably achievable (ALARA).

This PMR item continues to require that the headspace gas sample be taken using either the manifold method or the direct canister method as specified in Sections B1-1a(1) and B1-1a(2), respectively. This requirement also includes all of the appropriate cleaning and

quality control samples associated with the method being used (i.e., either manifold or direct canister).

The use of either sampling method (i. e., the airtight fitting or the self-taping screw) is subject to all of the existing reporting and auditing requirements in the Permit. This means a generator site that intends to use this sampling method is required to include it in their site-specific Quality Assurance Project Plan (QAPjP) and have that QAPjP approved by the Permittees and submitted to the NMED. In addition, the implementation of the sampling method is subject to the Permittees Auditing and Surveillance Program.

This PMR item establishes a methodology to assure that representative headspace gas samples are taken. This is accomplished by establishing additional requirements for taking headspace gas samples through an existing filter vent hole using an airtight sampling apparatus. Documentation that supports using an airtight seal to sample through an existing vent hole, including the reproducibility of the results, is included in Attachment D.

**Proposed Revised Permit Text:**

a. 1. Table of Contents

B1-1a(3) Sampling Heads . . . . .	B1-6
B1-1a(3)(i) Sampling Through the Carbon Filter . . . . .	B1-6
B1-1a(3)(ii) Sampling Through the Drum Lid <u>By Drum Punching</u> . . . . .	B1-7
<u>B1-1a(3)(iii) Sampling Through an Existing Filter Vent Hole. . . . .</u>	<u>B1-8</u>

a. 2. B1-1a(1) Manifold Headspace Gas Sampling

This headspace gas sampling protocol employs a multiport manifold capable of collecting multiple simultaneous headspace samples for analysis and QC purposes. The manifold can be used to collect samples in SUMMA® or equivalent canisters or as part of an on-line integrated sampling/analysis system. The sampling equipment will be leak checked and cleaned prior to first use and as needed thereafter. The manifold and sample canisters will be evacuated to 0.0039 inches (in.) (0.10 millimeters [mm]) mercury (Hg) prior to sample collection. Cleaned and evacuated sample canisters will be attached to the evacuated manifold before the manifold inlet valve is opened. The manifold inlet valve will be attached to a changeable filter connected to either a side port needle sampling head (for penetrating a filter) or a sampling head with an airtight seal for sampling through an existing filter vent hole, or a drum punch sampling head

(capable of punching through the metal lid of a drum).

a. 3. B1-1a(2) Direct Canister Headspace Gas Sampling

This headspace gas sampling protocol employs a canister-sampling system to collect headspace gas samples for analysis and QC purposes without the use of the manifold described above. Rather than attaching sampling heads to a manifold, in this method the sampling heads are attached directly to an evacuated sample canister as shown in Figure B1-3.

Canisters shall be evacuated to 0.0039 in. (0.10 mm) Hg prior to use and attached to a changeable filter connected to the appropriate sampling head. The sampling head(s) must be capable of punching through the metal lid of the drums, a sampling head with an airtight seal for sampling through the existing filter vent hole, or penetrating a filter, or penetrating the septum in the orifice of the self-tapping screw to obtain the drum headspace samples. Field duplicates must be collected at the same time, in the same manner, and using the same type of sampling apparatus as used for headspace-gas sample collection. Field blanks shall be samples of room air collected in the immediate vicinity of the waste-drum sampling area prior to removal of the drum lid. Equipment blanks and field-reference standards must be collected using a purge assembly equivalent to the standard side of the manifold described above. These samples shall be collected from the needle tip through the same components (e.g., needle and filter) that the headspace-gas samples pass through.

The sample canisters, associated sampling heads, and the headspace-sample volume requirements ensure that a representative sample is collected. When an estimate of the available headspace-gas volume of the waste container can be made, less than 10 percent of that volume should be withdrawn. A determination of the sampling head internal volume shall be made and documented. The total volume of headspace gases collected during each headspace gas sampling operation can be determined by adding the volume of the sample canister(s) attached to the sampling head to the internal volume of the sampling head. Every effort shall be made to minimize the internal volume of sampling heads.

Each sample canister used with the direct canister method shall have a pressure/vacuum gauge capable of indicating leaks and sample collection volumes. Canister gauges are intended to be gross leak-detection devices not vacuum-certification devices. If a canister pressure/vacuum gauge indicates an unexpected pressure change, determination of whether the change is a result of ambient temperature and pressure differences or a canister leak shall be made. This gauge shall be helium-leak tested to  $1.5 \times 10^{-7}$  standard cc/s, have all stainless steel construction, and be capable of tolerating temperatures to 125EC.

The SUMMA® or equivalent sample canisters as specified in EPA's Compendium Method TO-14 (EPA 1988) shall be used when sampling each drum. These heads shall form a leak-tight connection with the canister and allow sampling through the drum-lid filter, ~~or~~ through the drum lid itself (by use of punch, self-tapping screw), or using an airtight seal to collect a sample through the existing filter vent hole. Figure B1-3 illustrates the direct canister-sampling equipment.

a. 4. Section B1-1a(3)(ii) Sampling Through the Drum Lid By Drum Punching

Sampling through the drum lid at the time of drum punching or shortly thereafter may be performed as an alternative to sampling through the drum's filter if an airtight seal can be maintained. To sample the drum headspace-gas through the drum lid at the time of drum punching or shortly thereafter, the lid shall be breached using an appropriate punch. The punch shall form an airtight seal between the drum lid and the manifold or direct canister sampling equipment. To assure that the sample collected is representative, all of the general method requirements, sampling apparatus requirements, and QC requirements specified in EPA's Compendium Method TO-14 (EPA 1988) as appropriate, shall be met in addition to the following requirements:

- The seal between the drum lid and sampling head shall be designed to minimize intrusion of ambient air.
- c All components of the ~~drum-punch~~ sampling system that come into contact with sample gases shall be purged with humidified zero air, nitrogen, or helium prior to sample collection .

- C Equipment blanks and field reference standards shall be collected through all the components of the punch that contact the headspace-gas sample.
- C Pressure shall be applied to the punch until the drum lid has been breached.
- C Provisions shall be made to relieve ~~potential~~ excessive drum pressure increases during drum-punch operations; potential pressure increases may occur during sealing of the drum punch to the drum lid.
- C The lid of the drum's 90-mil poly liner shall contain a hole for venting to the drum. A representative sample cannot be collected until the poly-liner has been vented to the drum. If headspace-gas samples are collected prior to venting the 90-mil poly liner, the sample is not acceptable and a nonconformance report shall be prepared, submitted, and resolved. Nonconformance procedures are outlined in Permit Attachment B3.
- C During sampling, the drum's filter, if present, shall be sealed to prevent outside air from entering the drum.
- C While sampling through the drum lid using manifold sampling, a flow-indicating device or pressure regulator to verify ~~excess~~ flow of ~~QC~~ gases ~~(for system purge)~~ shall be pneumatically connected to the drum punch and operated in the same manner as the flow-indicating device described above in Section B1-1a(1).
- C Equipment shall be used to adequately secure the drum-punch sampling system to the drum lid.

a.5. Attachment B1-1a(3)(iii)

### B1-1a(3)(iii) Sampling Through an Existing Filter Vent Hole

Sampling through an existing filter vent hole may be performed as an alternative to sampling through the container's filter if an airtight seal can be maintained. To sample the container headspace-gas through an existing filter vent hole, an appropriate airtight seal shall be used. The sampling apparatus shall form an airtight seal between the container surface and the manifold or direct canister sampling equipment. To assure that the sample collected is representative, all of the general method, sampling apparatus, and QC requirements specified in EPA's Compendium Method TO-14 (EPA 1988) as appropriate, shall be met in addition to the following requirements:

- C The seal between the container surface and sampling apparatus shall be designed to minimize intrusion of ambient air.
- C The filter shall be replaced as quickly as is practicable with the airtight sampling apparatus to ensure that a representative sample can be taken.  
Generator/storage sites must provide documentation demonstrating that the time between removing the filter and installing the airtight sampling device has been established by testing to assure a representative sample.
- C All components of the sampling system that come into contact with sample gases shall be cleaned according to requirements for direct canister sampling or manifold sampling, whichever is appropriate, prior to sample collection.
- C Equipment blanks and field reference standards shall be collected through all the components of the sampling system that contact the headspace-gas sample.
- C The lid of the container's 90-mil poly liner shall contain a hole for venting to the container. A representative sample cannot be collected until the poly-liner has been vented to the container. If headspace-gas samples are collected prior to venting the 90-mil poly liner, the sample is not acceptable and a nonconformance report shall be prepared, submitted, and resolved.



Nonconformance procedures are outlined in Permit Attachment B3. Note, as an option, the same airtight seal sampling apparatus may include a needle to penetrate the rigid liner.

C During sampling, openings in the container shall be sealed to prevent outside air from entering the container.

C A flow-indicating device shall be connected to sampling system and operated according to the direct canister or manifold sampling requirements, as appropriate.

#### a. 6. B1-1c(5) Sampling Head Cleaning

To prevent cross contamination, the needle or airtight seal, adapters, and filter of the sampling heads shall be cleaned in accordance with the cleaning procedures described in EPA's Compendium Method TO-14 (EPA 1988). After sample collection, a sampling head shall be disposed of or cleaned in accordance with EPA's Compendium Method TO-14 (EPA 1988), prior to reuse. As a further QC measure, the needle or airtight seal, and filter, after cleaning, should be purged with zero air, nitrogen, or helium and capped for storage to prevent sample contamination by VOCs potentially present in ambient air.

#### b.1. B6 – Table B6-4

<u>190</u>	<p>Are procedures, processes, and equipment in place to ensure that the following manifold sampling procedures are implemented:</p> <ul style="list-style-type: none"> <li>C The sampling equipment is leak checked and cleaned upon first use and as needed</li> <li>C The manifold and sample canisters are evacuated to 0.1 mm Hg prior to sample collection</li> <li>C Cleaned and evacuated sample canisters are attached to the evacuated manifold before the manifold inlet valve is opened</li> <li>C The manifold inlet valve is attached to a changeable filter connected to different sampling heads that are capable of punching through the metal lid of the drum <u>or providing an airtight seal when sampling through the existing filter vent hole</u>, or penetrating the <del>carbon-composite</del> filter</li> </ul>
------------	---

	<p>C Field blanks are collected using samples of room air collected in the sampling area in the immediate vicinity of the waste container:</p> <p><i>(Note: field blanks for SUMMA® canisters are collected directly into the canister)</i></p> <p>C Manifold equipped with purge assembly that allows QC samples to be collected through all sampling components that affect compliance with QAOs</p> <p>C The manifold internal volume is calculated and documented in a field logbook</p> <p>C The volume of headspace gas collected as calculated by the canister volume and internal manifold volume is less than 10 percent of the available headspace volume when a volume estimate is available</p> <p>(Section B1-1a(1))</p>
--	---

b.2. B6 – Table B6-5

<u>195</u>	<p>Are procedures, processes, and equipment in place to ensure that the following operating conditions are in place for direct canister sampling:</p> <p>C Canisters are evacuated to 0.1 mm Hg prior to use and attached to a changeable filter connected to the sampling head</p> <p>C Sampling heads are capable of punching through the metal lid of the drums; <u>providing an airtight seal when sampling through the existing filter vent hole,</u> or penetrating a <del>carbon composite</del> filter, <u>or penetrating the septum in the orifice of a self-tapping screw</u></p> <p>C Field duplicates are collected in the same manner and at the same time as the original sample:</p> <p>C Field blanks shall be samples of room air collected in the immediate vicinity of the waste drum sampling area prior to removal of the drum lid:</p> <p>C Equipment blanks and field reference standards shall be collected using a purge assembly equivalent to the standard side of the manifold</p> <p>C Less than 10 percent of the headspace is withdrawn when a headspace estimate is available</p> <p><i>(Note: The volume withdrawn is the canister volume and the internal volume</i></p>	<p>↓</p> <p> </p> <p> </p>
------------	--	----------------------------

	<p><i>of the sampling head)</i></p> <p>c Each sample canister is equipped with a pressure/vacuum gauge capable of indicating leaks and sample collection volumes. The gauge shall be helium-leak tested to <math>1.5 \times 10^{-7}</math> standard cc/s, have all stainless steel construction, and be capable of tolerating temperatures to 125°C</p> <p>c SUMMA® canisters or equivalent are used to collect samples</p> <p>(Section B1-1a(2))</p>
--	---

b. 3. B6 - Table B6-5

<u>197a</u>	<p><u>If sampling through an existing filter vent hole with an airtight device is used, are procedures in place to ensure that a sampling head with an airtight seal for sampling through an existing filter vent hole is available?</u></p> <p><u>(Section B1-1a(1); B1-1a(2); B1-1c(5))</u></p>
<u>197b</u>	<p><u>If Sampling through an existing filter vent hole is used, are the following criteria met:</u></p> <p><u>c The seal between the container surface and sampling apparatus shall be designed to minimize intrusion of ambient air.</u></p> <p><u>c The filter shall be replaced as quickly as is practicable with the airtight sampling apparatus to ensure that a representative sample can be taken.</u></p> <p><u>c All components of the sampling system that come into contact with sample gases shall be cleaned according to requirements for direct canister sampling or manifold sampling, whichever is appropriate, prior to sample collection.</u></p> <p><u>c Equipment blanks and field reference standards shall be collected through all the components of the sampling system that contact the headspace-gas sample.</u></p> <p><u>c The lid of the container's 90-mil poly liner shall contain a hole for venting to the container. A representative sample cannot be collected until the poly-liner has been vented to the container. If headspace-gas samples are collected prior to venting the 90-mil poly liner, the sample is not acceptable and a nonconformance report shall be prepared, submitted, and resolved. Nonconformance procedures are outlined in Permit Attachment B3. Note, as an option, the same airtight seal sampling apparatus may include a needle to penetrate the rigid liner.</u></p> <p><u>c During sampling, openings in the container shall be sealed to</u></p>

	<p><u>prevent outside air from entering the container.</u></p> <p><u>C</u> <u>A flow-indicating device shall be connected to sampling system and operated according to the direct canister or manifold sampling requirements, as appropriate.</u></p> <p><u>(Section B1-1a(3)(iii))</u></p>
<u>197c</u>	<p><u>If Sampling through an existing filter vent hole is used, are the following criteria met, does the site must have documentation that demonstrates that they have determined through testing the appropriate length of time for exchanging the filter with the sampling device to assure representative samples are collected.</u></p> <p><u>Is the time for completing the exchange incorporated into appropriate headspace gas sampling procedures.</u></p> <p><u>(Section B1-1a(3)(iii))</u></p>

**Attachment B**  
**INFORMATION SUPPORTING ITEM 1**

**SW-846 METHOD 8260**

**e-MAIL RESPONSE FROM THE METHODS INFORMATION COMMUNICATION  
EXCHANGE REGARDING METHOD 8260 COMPOSITING**

**TECHNICAL EVALUATION OF HEADSPACE GAS COMPOSITING**

**SW-846 METHOD 8260**

METHOD 8260B  
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/  
MASS SPECTROMETRY (GC/MS)

## 1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Compound	CAS No. <sup>b</sup>	Appropriate Preparation Technique <sup>a</sup>					Direct Inject.
		5030/ 5035	5031	5032	5021	5041	
Acetone	67-64-1	pp	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	nd	c
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	c	c
4-Bromofluorobenzene (surr)	460-00-4	c	nd	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c
t-Butyl alcohol	75-65-0	pp	c	nd	nd	nd	c
Carbon disulfide	75-15-0	pp	nd	c	nd	c	c
Carbon tetrachloride	56-23-5	c	nd	c	c	c	c
Chloral hydrate	302-17-0	pp	nd	nd	nd	nd	c
Chlorobenzene	108-90-7	c	nd	c	c	c	c
Chlorobenzene-d <sub>5</sub> (IS)		c	nd	c	c	c	c
Chlorodibromomethane	124-48-1	c	nd	c	nd	c	c
Chloroethane	75-00-3	c	nd	c	c	c	c
2-Chloroethanol	107-07-3	pp	nd	nd	nd	nd	c
2-Chloroethyl vinyl ether	110-75-8	c	nd	c	nd	nd	c
Chloroform	67-66-3	c	nd	c	c	c	c
Chloromethane	74-87-3	c	nd	c	c	c	c
Chloroprene	126-99-8	c	nd	nd	nd	nd	c
3-Chloropropionitrile	542-76-7	l	nd	nd	nd	nd	pc

(continued)

Compound	CAS No. <sup>b</sup>	Appropriate Preparation Technique <sup>a</sup>					Direct Inject.
		5030/ 5035	5031	5032	5021	5041	
Crotonaldehyde	4170-30-3	pp	c	nd	nd	nd	c
1,2-Dibromo-3-chloropropane	96-12-8	pp	nd	nd	c	nd	c
1,2-Dibromoethane	106-93-4	c	nd	nd	c	nd	c
Dibromomethane	74-95-3	c	nd	c	c	c	c
1,2-Dichlorobenzene	95-50-1	c	nd	nd	c	nd	c
1,3-Dichlorobenzene	541-73-1	c	nd	nd	c	nd	c
1,4-Dichlorobenzene	106-46-7	c	nd	nd	c	nd	c
1,4-Dichlorobenzene-d <sub>4</sub> (IS)		c	nd	nd	c	nd	c
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd	c	nd	nd	c
trans-1,4-Dichloro-2-butene	110-57-6	pp	nd	c	nd	nd	c
Dichlorodifluoromethane	75-71-8	c	nd	c	c	nd	c
1,1-Dichloroethane	75-34-3	c	nd	c	c	c	c
1,2-Dichloroethane	107-06-2	c	nd	c	c	c	c
1,2-Dichloroethane-d <sub>4</sub> (surr)		c	nd	c	c	c	c
1,1-Dichloroethene	75-35-4	c	nd	c	c	c	c
trans-1,2-Dichloroethene	156-60-5	c	nd	c	c	c	c
1,2-Dichloropropane	78-87-5	c	nd	c	c	c	c
1,3-Dichloro-2-propanol	96-23-1	pp	nd	nd	nd	nd	c
cis-1,3-Dichloropropene	10061-01-5	c	nd	c	nd	c	c
trans-1,3-Dichloropropene	10061-02-6	c	nd	c	nd	c	c
1,2,3,4-Diepoxybutane	1464-53-5	c	nd	nd	nd	nd	c
Diethyl ether	60-29-7	c	nd	nd	nd	nd	c
1,4-Difluorobenzene (IS)	540-36-3	nd	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	pp	c	c	nd	nd	c
Epichlorohydrin	106-89-8	l	nd	nd	nd	nd	c
Ethanol	64-17-5	l	c	c	nd	nd	c
Ethyl acetate	141-78-6	l	c	nd	nd	nd	c
Ethylbenzene	100-41-4	c	nd	c	c	c	c
Ethylene oxide	75-21-8	pp	c	nd	nd	nd	c
Ethyl methacrylate	97-63-2	c	nd	c	nd	nd	c
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	l	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
2-Hydroxypropionitrile	78-97-7	l	nd	nd	nd	nd	pc
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	pp	c	nd	nd	nd	c
Isopropylbenzene	98-82-8	c	nd	nd	c	nd	c
Malononitrile	109-77-3	pp	nd	nd	nd	nd	c
Methacrylonitrile	126-98-7	pp	l	nd	nd	nd	c
Methanol	67-56-1	l	c	nd	nd	nd	c
Methylene chloride	75-09-2	c	nd	c	c	c	c
Methyl methacrylate	80-62-6	c	nd	nd	nd	nd	c
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	c	c	nd	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c

(continued)



Compound	CAS No. <sup>b</sup>	Appropriate Preparation Technique <sup>a</sup>					Direct Inject.
		5030/ 5035	5031	5032	5021	5041	
Nitrobenzene	98-95-3	c	nd	nd	nd	nd	c
2-Nitropropane	79-46-9	c	nd	nd	nd	nd	c
N-Nitroso-di-n-butylamine	924-16-3	pp	c	nd	nd	nd	c
Paraldehyde	123-63-7	pp	c	nd	nd	nd	c
Pentachloroethane	76-01-7	l	nd	nd	nd	nd	c
2-Pentanone	107-87-9	pp	c	nd	nd	nd	c
2-Picoline	109-06-8	pp	c	nd	nd	nd	c
1-Propanol	71-23-8	pp	c	nd	nd	nd	c
2-Propanol	67-63-0	pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	l	nd	nd	nd	c
β-Propiolactone	57-57-8	pp	nd	nd	nd	nd	c
Propionitrile (ethyl cyanide)	107-12-0	ht	c	nd	nd	nd	pc
n-Propylamine	107-10-8	c	nd	nd	nd	nd	c
Pyridine	110-86-1	l	c	nd	nd	nd	c
Styrene	100-42-5	c	nd	c	c	c	c
1,1,1,2-Tetrachloroethane	630-20-6	c	nd	nd	c	c	c
1,1,2,2-Tetrachloroethane	79-34-5	c	nd	c	c	c	c
Tetrachloroethene	127-18-4	c	nd	c	c	c	c
Toluene	108-88-3	c	nd	c	c	c	c
Toluene-d <sub>8</sub> (surr)	2037-26-5	c	nd	c	c	c	c
o-Toluidine	95-53-4	pp	c	nd	nd	nd	c
1,2,4-Trichlorobenzene	120-82-1	c	nd	nd	c	nd	c
1,1,1-Trichloroethane	71-55-6	c	nd	c	c	c	c
1,1,2-Trichloroethane	79-00-5	c	nd	c	c	c	c
Trichloroethene	79-01-6	c	nd	c	c	c	c
Trichlorofluoromethane	75-69-4	c	nd	c	c	c	c
1,2,3-Trichloropropane	96-18-4	c	nd	c	c	c	c
Vinyl acetate	108-05-4	c	nd	c	nd	nd	c
Vinyl chloride	75-01-4	c	nd	c	c	c	c
o-Xylene	95-47-6	c	nd	c	c	c	c
m-Xylene	108-38-3	c	nd	c	c	c	c
p-Xylene	106-42-3	c	nd	c	c	c	c

<sup>a</sup> See Sec. 1.2 for other appropriate sample preparation techniques

<sup>b</sup> Chemical Abstract Service Registry Number

c = Adequate response by this technique  
 ht = Method analyte only when purged at 80°C  
 nd = Not determined  
 l = Inappropriate technique for this analyte  
 pc = Poor chromatographic behavior  
 pp = Poor purging efficiency resulting in high Estimated Quantitation Limits  
 surr = Surrogate  
 IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene	1,3-Dichloropropane
n-Butylbenzene	2,2-Dichloropropane
sec-Butylbenzene	1,1-Dichloropropene
tert-Butylbenzene	p-Isopropyltoluene
Chloroacetonitrile	Methyl acrylate
1-Chlorobutane	Methyl-t-butyl ether
1-Chlorohexane	Pentafluorobenzene
2-Chlorotoluene	n-Propylbenzene
4-Chlorotoluene	1,2,3-Trichlorobenzene
Dibromofluoromethane	1,2,4-Trimethylbenzene
cis-1,2-Dichloroethene	1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrupole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

## 2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

## 3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explain this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

#### 4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

#### 4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

#### 4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt<sub>x</sub>-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt<sub>x</sub>-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at  $m/z$  49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000- $\mu$ L.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

- 4.15 Vials - 2-mL, for GC autosampler.
- 4.16 Disposable pipets - Pasteur.
- 4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.
- 4.18 Spatula - Stainless steel.

## 5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol,  $\text{CH}_3\text{OH}$  - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol,  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$  - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100- $\mu\text{L}$  syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below  $30^\circ\text{C}$  (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

#### 5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

#### 5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.



5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

- a) Connect either the 100- $\mu$ L or 500- $\mu$ L Luer syringe to the inlet fitting of the cylinder.
- b) Make sure the on/off valve on the syringe is in the open position.
- c) Slowly open the valve on the cylinder and withdraw a full syringe volume.
- d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.
- e) Expel the gas from the syringe into a well-ventilated area.
- f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025  $\mu$ g/ $\mu$ L.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

<u>Gas Volume</u>	<u>Calibration Concentration</u>
40 $\mu$ L	20 $\mu$ g/L
100 $\mu$ L	50 $\mu$ g/L
200 $\mu$ L	100 $\mu$ g/L
300 $\mu$ L	150 $\mu$ g/L
400 $\mu$ L	200 $\mu$ g/L

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

<u>Gas Volume</u>	<u>Calibration Concentration</u>
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-d<sub>8</sub>, 4-bromofluorobenzene, 1,2-dichloroethane-d<sub>4</sub>, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d<sub>5</sub>, and 1,4-dichlorobenzene-d<sub>4</sub>. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards - There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

## 7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

## 7.2 Recommended chromatographic conditions

### 7.2.1 General conditions

Injector temperature:	200 - 225°C
Transfer line temperature:	250 - 300°C

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

#### 7.2.5 Direct injection - Column 2

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-624, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out:	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

#### 7.2.6 Direct split interface - Column 4

Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	4°C/min to 50°C
	10°C/min to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted
Split ratio:	100:1
Injector temperature:	125°C

### 7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	35 - 260 amu
Scan time:	0.6 - 2 sec/scan
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

**NOTE:** All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10  $\mu$ L of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2  $\mu$ L into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

$A_s$  = Peak area (or height) of the analyte or surrogate.

$A_{is}$  = Peak area (or height) of the internal standard.

$C_s$  = Concentration of the analyte or surrogate.

$C_{is}$  = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion ( $m/z$  173) is directly affected by the tuning of BFB at ions  $m/z$  174/176. Increasing the  $m/z$  174/176 ratio relative to  $m/z$  95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

#### 7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^n (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

$RF_i$  = RF for each of the calibration standards

$\overline{RF}$  = mean RF for each compound from the initial calibration

$n$  = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

1,1-Dichloroethene  
Chloroform  
1,2-Dichloropropane

Toluene  
Ethylbenzene  
Vinyl chloride

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

#### 7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

**NOTE:** Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.



NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

#### 7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

#### 7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

## 7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10  $\mu\text{L}$  of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50  $\mu\text{g/L}$  of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2  $\mu\text{L}$  into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2  $\mu\text{L}$  injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

**NOTE:** It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

## 7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within  $\pm 0.06$  RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

- (1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- (2) The relative intensities of the major ions should agree within  $\pm 20\%$ . (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
- (3) Molecular ions present in the reference spectrum should be present in the sample spectrum.
- (4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- (5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

## 7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor ( $\overline{RF}$ ) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas  $A_x$  and  $A_{is}$  should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each



sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

## 10.0 REFERENCES

1. Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water Method 524.2, U.S. Environmental Protection Agency, Office of Research Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.
2. Bellar, T.A., Lichtenberg, J.J., J. Amer. Water Works Assoc., 1974, 66(12), 739-744.
3. Bellar, T.A., Lichtenberg, J.J., "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds"; in Van Hall, Ed.; Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.
4. Budde, W.L., Eichelberger, J.W., "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, April 1980; EPA-600/4-79-020.
5. Eichelberger, J.W., Harris, L.E., Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems"; Analytical Chemistry 1975, 47, 995-1000.
6. Olynyk, P., Budde, W.L., Eichelberger, J.W., "Method Detection Limit for Methods 624 and 625"; Unpublished report, October 1980.
7. Non Cryogenic Temperatures Program and Chromatogram, Private Communications; M. Stephenson and F. Allen, EPA Region IV Laboratory, Athens, GA.
8. Marsden, P.J., Helms, C.L., Colby, B.N., "Analysis of Volatiles in Waste Oil"; Report for B. Lesnik, OSW/EPA under EPA contract 68-W9-001, 6/92.
9. Methods for the Determination of Organic Compounds in Drinking Water, Supplement II Method 524.2; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1992.
10. Flores, P., Bellar, T., "Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, December, 1992.
11. Bruce, M.L., Lee, R.P., Stephens, M.W., "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environmental Science and Technology 1992, 26, 160-163.
12. Cramer, P.H., Wilner, J., Stanley, J.S., "Final Report: Method for Polar, Water Soluble, Nonpurgeable Volatile Organics (VOCs)", For U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, EPA Contract No. 68-C8-0041.

13. Hiatt, M.H., "Analysis of Fish and Sediment for Volatile Priority Pollutants", Analytical Chemistry 1981, 53, 1541.
14. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.
15. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)  
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes)			MDL <sup>d</sup> (µg/L)
	Column 1 <sup>a</sup>	Column 2 <sup>b</sup>	Column 2 <sup>c</sup>	
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	5.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--

TABLE 1 (cont.)

Compound	Retention Time (minutes)			MDL <sup>d</sup> (µg/L)
	Column 1 <sup>a</sup>	Column 2 <sup>b</sup>	Column 2 <sup>nc</sup>	
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10
Ethyl methacrylate	20.01			
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	--	13.29	--	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	--	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1 (cont.)

Compound	Retention Time (minutes)			MDL <sup>d</sup> (µg/L)
	Column 1 <sup>a</sup>	Column 2 <sup>b</sup>	Column 2 <sup>nc</sup>	
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d <sub>5</sub>	23.10			
1,4-Dichlorobenzene-d <sub>4</sub>	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d <sub>4</sub>	32.30	19.08	27.25	
Dichloroethane-d <sub>4</sub>	12.08			
Dibromofluoromethane	--			
Toluene-d <sub>8</sub>	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

<sup>a</sup> Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

<sup>b</sup> Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

<sup>c</sup> Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

<sup>d</sup> MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)  
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 3 <sup>a</sup>	MDL <sup>b</sup> (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06

TABLE 2 (cont.)

Compound	Retention Time (minutes) Column 3 <sup>a</sup>	MDL <sup>b</sup> (µg/L)
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

<sup>a</sup> Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

<sup>b</sup> MDL based on a 25-mL sample volume.



TABLE 3  
ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES<sup>a</sup>

Estimated Quantitation Limits		
5-mL Ground Water Purge (µg/L)	25-mL Ground water Purge (µg/L)	Low Soil/Sediment <sup>b</sup> µg/kg
5	1	5

<sup>a</sup> Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

<sup>b</sup> EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor <sup>c</sup>
Water miscible liquid waste	50
High concentration soil and sludge	125
Non-water miscible waste	500

<sup>c</sup> EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA<sup>a</sup>

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

<sup>a</sup> Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 5

## CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d <sub>4</sub>	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
$\beta$ -Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d <sub>6</sub>	84	83
Bromobenzene-d <sub>5</sub>	82	162
Bromochloromethane-d <sub>2</sub>	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d <sub>5</sub>	117	
1,4-Dichlorobenzene-d <sub>4</sub>	152	115, 150
1,1,2-Trichloroethane-d <sub>3</sub>	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d <sub>1</sub>	84	
Dibromofluoromethane	113	

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d <sub>4</sub>	102	
Toluene-d <sub>8</sub>	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

\* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR  
PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED  
WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery <sup>a</sup>	Standard Deviation of Recovery <sup>b</sup>	RSD
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3

TABLE 6 (cont.)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery <sup>a</sup>	Standard Deviation of Recovery <sup>b</sup>	RSD
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

<sup>a</sup> Recoveries were calculated using internal standard method. The internal standard was fluorobenzene.

<sup>b</sup> Standard deviation was calculated by pooling data from three concentrations.



TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR  
PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED  
WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. (µg/L)	Number of Samples	% Recovery <sup>a</sup>	Standard Deviation of Recovery <sup>b</sup>	RSD
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.5	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3

TABLE 7 (cont.)

Compound	Conc. (µg/L)	Number of Samples	% Recovery <sup>a</sup>	Standard Deviation of Recovery <sup>b</sup>	RSD
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

<sup>a</sup> Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

## SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Water	Soil/Sediment
4-Bromofluorobenzene <sup>a</sup>	86-115	74-121
Dibromofluoromethane <sup>a</sup>	86-118	80-120
Toluene-d <sub>8</sub> <sup>a</sup>	88-110	81-117
Dichloroethane-d <sub>4</sub> <sup>a</sup>	80-120	80-120

<sup>a</sup> Single laboratory data, for guidance only.

TABLE 9

## QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

Approximate Concentration Range (µg/kg)	Volume of Extract <sup>a</sup>
500 - 10,000	100 µL
1,000 - 20,000	50 µL
5,000 - 100,000	10 µL
25,000 - 500,000	100 µL of 1/50 dilution <sup>b</sup>

Calculate appropriate dilution factor for concentrations exceeding this table.

<sup>a</sup> The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

<sup>b</sup> Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

## DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Trichlorotrifluoroethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

\* Alternate mass employed

\*\* IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE  
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone**	105	54	2.0	5.0
Benzene	3135	44	14	0.5
Benzene-d <sub>6</sub>	56	44	2.9	0.5
n-Butanol**	100	71	12	5.0
iso-Butanol*, **	132	27	0	5.0
Carbon tetrachloride	143	68	0	0.5
Carbon tetrachloride- <sup>13</sup> C	99	44	5.1	0.5
Carbon disulfide**	95	63	0	5.0
Chlorobenzene	148	71	0	5.0
Chlorobenzene-d <sub>5</sub>	60	44	3.6	5.0
Chloroform	149	74	0	6.0
Chloroform-d <sub>1</sub>	51	44	2.6	6.0
1,4-Dichlorobenzene	142	72	0	7.5
1,4-Dichlorobenzene-d <sub>4</sub>	53	44	3.4	7.5
1,2-Dichloroethane**	191	54	0	0.5
1,1-Dichloroethene*	155	51	0	0.7
1,1-Dichloroethene-d <sub>2</sub>	68	44	3.4	0.7
Diethyl ether**	95	66	0	5.0
Ethyl acetate*, **	126	39	0	5.0
Ethylbenzene	1298	44	54	5.0
Ethylbenzene-d <sub>10</sub>	63	44	3.6	5.0
Hexachloroethane	132	72	0	3.0
Hexachloroethane- <sup>13</sup> C	54	45	3.5	3.0
Methylene chloride**	86	65	0.3	5.0
Methyl ethyl ketone**	107	64	0	5.0
4-Methyl-2-pentanone (MIBK)**	100	74	0.1	5.0
Nitrobenzene	111	80	0	2.0
Nitrobenzene-d <sub>5</sub>	65	53	4.0	2.0
Pyridine**	68	85	0	5.0
Pyridine-d <sub>5</sub>	ND	--	0	5.0
Tetrachloroethene**	101	73	0	0.7
Trichlorofluoromethane**	91	70	0	5.0
1,1,2-Cl <sub>3</sub> F <sub>3</sub> ethane**	81	70	0	5.0
Toluene	2881	44	128	5.0
Toluene-d <sub>8</sub>	63	44	3.6	5.0
Trichloroethene	152	57	0	0.5
Trichloroethene-d <sub>1</sub>	55	44	2.8	0.5

TABLE 11 (cont.)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Vinyl chloride**	100	69	0	0.2
o-Xylene	2292	44	105	5.0
o-Xylene-d <sub>10</sub>	76	44	4.2	5.0
m-/p-Xylene	2583	44	253	10.0
p-Xylene-d <sub>10</sub>	67	44	3.7	10.0

\* Alternate mass employed

\*\* IS quantitation

ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

TABLE 12  
METHOD DETECTION LIMITS (METHOD 5031)

Compound	MDL (µg/L)	Concentration Factor	
	Macro <sup>a</sup>	Macro	Micro
Acetone	31	25-500	-
Acetonitrile	57	25-500	200
Acrolein	-	-	100
Acrylonitrile	16	25-500	100
Allyl Alcohol	7	25-500	-
1-Butanol	-	-	250
Crotonaldehyde	12	25-500	-
1,4-Dioxane	12	25-500	150
Ethyl Acetate	-	-	100
Isobutyl alcohol	7	25-500	-
Methanol	38	25-500	140
Methyl Ethyl Ketone	16	25-500	-
2-Methyl-1-propanol	-	-	250
n-Nitroso-di-n-butylamine	14	25-500	-
Paraldehyde	10	25-500	-
2-Picoline	7	25-500	-
1-Propanol	-	-	240
Propionitrile	11	25-500	200
Pyridine	4	25-500	-
o-Toluidine	13	25-500	-

<sup>a</sup> Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

$$\text{MDL} = 3.134 \times \text{Std. Dev. of low concentration spike (ppb)}.$$

<sup>b</sup> When a 40-mL sample is used, and the first 100 µL of distillate are collected.

TABLE 13

## TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

Target Compound	Surrogate	Internal Standard
Acetone	d <sub>6</sub> -Acetone	d <sub>8</sub> -Isopropyl alcohol
Acetonitrile	d <sub>3</sub> -Acetonitrile	d <sub>8</sub> -Isopropyl alcohol
Acrylonitrile	d <sub>8</sub> -Isopropyl alcohol	
Allyl alcohol	d <sub>7</sub> -Dimethyl formamide	
Crotonaldehyde	d <sub>8</sub> -Isopropyl alcohol	
1,4-Dioxane	d <sub>8</sub> -1,4-Dioxane	d <sub>7</sub> -Dimethyl formamide
Isobutyl alcohol	d <sub>7</sub> -Dimethyl formamide	
Methanol	d <sub>3</sub> -Methanol	d <sub>8</sub> -Isopropyl alcohol
Methyl ethyl ketone	d <sub>8</sub> -Isopropyl alcohol	
N-Nitroso-di-n-butylamine	d <sub>7</sub> -Dimethyl formamide	
Paraldehyde	d <sub>7</sub> -Dimethyl formamide	
2-Picoline	d <sub>7</sub> -Dimethyl formamide	
Propionitrile	d <sub>8</sub> -Isopropyl alcohol	
Pyridine	d <sub>5</sub> -Pyridine	d <sub>7</sub> -Dimethyl formamide
o-Toluidine	d <sub>7</sub> -Dimethyl formamide	



TABLE 14

## RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

Compound	Concentration(s) (ng/μL)
Internal Standards	
d <sub>5</sub> -benzyl alcohol	10.0
d <sub>14</sub> -Diglyme	10.0
d <sub>7</sub> -Dimethyl formamide	10.0
d <sub>8</sub> -Isopropyl alcohol	10.0
Surrogates	
d <sub>6</sub> -Acetone	10.0
d <sub>3</sub> -Acetonitrile	10.0
d <sub>8</sub> -1,4-Dioxane	10.0
d <sub>3</sub> -Methanol	10.0
d <sub>5</sub> -Pyridine	10.0
Target Compounds	
Acetone	1.0, 5.0, 10.0, 25.0, 100.0
Acetonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Acrylonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Allyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Crotonaldehyde	1.0, 5.0, 10.0, 25.0, 100.0
1,4-Dioxane	1.0, 5.0, 10.0, 25.0, 100.0
Isobutyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Methanol	1.0, 5.0, 10.0, 25.0, 100.0
Methyl ethyl ketone	1.0, 5.0, 10.0, 25.0, 100.0
N-Nitroso-di-n-butylamine	1.0, 5.0, 10.0, 25.0, 100.0
Paraldehyde	1.0, 5.0, 10.0, 25.0, 100.0
2-Picoline	1.0, 5.0, 10.0, 25.0, 100.0
Propionitrile	1.0, 5.0, 10.0, 25.0, 100.0
Pyridine	1.0, 5.0, 10.0, 25.0, 100.0
o-Toluidine	1.0, 5.0, 10.0, 25.0, 100.0

TABLE 15

## CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

Compound	Quantitation Ion <sup>a</sup>	Secondary Ions	Retention Time (min) <sup>b</sup>
Internal Standards			
d <sub>8</sub> -Isopropyl alcohol	49		1.75
d <sub>14</sub> -Diglyme	66	98,64	9.07
d <sub>7</sub> -Dimethyl formamide	50	80	9.20
Surrogates			
d <sub>6</sub> -Acetone	46	64,42	1.03
d <sub>3</sub> -Methanol	33	35,30	1.75
d <sub>3</sub> -Acetonitrile	44	42	2.63
d <sub>8</sub> -1,4-Dioxane	96	64,34	3.97
d <sub>5</sub> -Pyridine	84	56,79	6.73
d <sub>5</sub> -Phenol <sup>c</sup>	99	71	15.43
Target Compounds			
Acetone	43	58	1.05
Methanol	31	29	1.52
Methyl ethyl ketone	43	72,57	1.53
Methacrylonitrile <sup>c</sup>	67	41	2.38
Acrylonitrile	53	52,51	2.53
Acetonitrile	41	40,39	2.73
Methyl isobutyl ketone <sup>c</sup>	85	100,58	2.78
Propionitrile	54	52,55	3.13
Crotonaldehyde	41	70	3.43
1,4-Dioxane	58	88,57	4.00
Paraldehyde	45	89	4.75
Isobutyl alcohol	43	33,42	5.05
Allyl alcohol	57	39	5.63
Pyridine	79	50,52	6.70
2-Picoline	93	66	7.27
N-Nitroso-di-n-butylamine	84	116	12.82
Aniline <sup>c</sup>	93	66,92	13.23
o-Toluidine	106	107	13.68
Phenol <sup>c</sup>	94	66,65	15.43

<sup>a</sup> These ions were used for quantitation in selected ion monitoring.

<sup>b</sup> GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.  
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.

<sup>c</sup> Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT  
RELATIVE STANDARD DEVIATION<sup>a</sup> (METHOD 5031 - MACRODISTILLATION TECHNIQUE)  
(Single Laboratory and Single Operator)

Compound	<u>25 ppb Spike</u>		<u>100 ppb Spike</u>		<u>500 ppb Spike</u>	
	Mean %R	%RSD	Mean %R	%RSD	Mean %R	%RSD
d <sub>6</sub> -Acetone	66	24	69	14	65	16
d <sub>3</sub> -Acetonitrile	89	18	80	18	70	10
d <sub>8</sub> -1,4-Dioxane	56	34	58	11	61	18
d <sub>3</sub> -Methanol	43	29	48	19	56	14
d <sub>5</sub> -Pyridine	83	6.3	84	7.8	85	9.0
Acetone	67	45	63	14	60	14
Acetonitrile	44	35	52	15	56	15
Acrylonitrile	49	42	47	27	45	27
Allyl alcohol	69	13	70	9.7	73	10
Crotonaldehyde	68	22	68	13	69	13
1,4-Dioxane	63	25	55	16	54	13
Isobutyl alcohol	66	14	66	5.7	65	7.9
Methanol	50	36	46	22	49	18
Methyl ethyl ketone	55	37	56	20	52	19
N-Nitroso-di- n-butylamine	57	21	61	15	72	18
Paraldehyde	65	20	66	11	60	8.9
Picoline	81	12	81	6.8	84	8.0
Propionitrile	67	22	69	13	68	13
Pyridine	74	7.4	72	6.7	74	7.3
o-Toluidine	52	31	54	15	58	12

<sup>a</sup> Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrupole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng)					Mean	RSD	Mean Rec
	1	2	3	4	5			
Vinyl chloride	8.0	7.5	6.7	5.4	6.6	6.8	13.0	34.2
Trichlorofluoromethane	13.3	16.5	14.9	13.0	10.3	13.6	15.2	68.0
1,1-Dichloroethene	17.1	16.7	15.1	14.8	15.6	15.9	5.7	79.2
Methylene chloride	24.5	22.7	19.7	19.4	20.6	21.4	9.1	107
trans-1,2-Dichloroethene	22.7	23.6	19.4	18.3	20.1	20.8	0.7	104
1,2-Dichloroethane	18.3	18.0	16.7	15.6	15.9	16.9	6.4	84.4
cis-1,2-Dichloroethene	26.1	23.1	22.6	20.3	20.8	22.6	9.0	113
Bromochloromethane	24.5	25.4	20.9	20.1	20.1	22.2	10.2	111
Chloroform	26.5	26.0	22.1	18.9	22.1	23.1	12.2	116
1,1,1-Trichloroethane	21.5	23.0	23.9	16.7	31.2	23.4	21.2	117
Carbon tetrachloride	23.6	24.2	22.6	18.3	23.3	22.4	9.4	112
Benzene	22.4	23.9	20.4	17.4	19.2	20.7	11.2	103
Trichloroethene	21.5	20.5	19.2	14.4	19.1	18.9	12.7	94.6
1,2-Dichloropropane	24.9	26.3	23.1	19.0	23.3	23.3	10.5	117
Dibromomethane	25.4	26.4	21.6	20.4	23.6	23.5	9.6	117
Bromodichloromethane	25.7	26.7	24.1	17.9	23.0	23.5	13.1	117
Toluene	28.3	25.0	24.8	16.3	23.6	23.6	16.9	118
1,1,2-Trichloroethane	25.4	24.5	21.6	17.7	22.1	22.2	12.1	111
1,3-Dichloropropane	25.4	24.2	22.7	17.0	22.2	22.3	12.8	112
Dibromochloromethane	26.3	26.2	23.7	18.2	23.2	23.5	12.5	118
Chlorobenzene	22.9	22.5	19.8	14.6	19.4	19.9	15.0	99.3
1,1,1,2-Tetrachloroethane	22.4	27.7	25.1	19.4	22.6	23.4	12.0	117
Ethylbenzene	25.6	25.0	22.1	14.9	24.0	22.3	17.5	112
p-Xylene	22.5	22.0	19.8	13.9	20.3	19.7	15.7	98.5
o-Xylene	24.2	23.1	21.6	14.0	20.4	20.7	17.3	103
Styrene	23.9	21.5	20.9	14.3	20.5	20.2	15.7	101
Bromoform	26.8	25.6	26.0	20.1	23.5	24.4	9.9	122
iso-Propylbenzene	25.3	25.1	24.2	15.4	24.6	22.9	16.6	114
Bromobenzene	19.9	21.8	20.0	15.5	19.1	19.3	10.7	96.3
1,2,3-Trichloropropane	25.9	23.0	25.6	15.9	21.4	22.2	15.8	111
n-Propylbenzene	26.0	23.8	22.6	13.9	21.9	21.6	19.0	106
2-Chlorotoluene	23.6	23.8	21.3	13.0	21.5	20.6	19.2	103
4-Chlorotoluene	21.0	19.7	18.4	12.1	18.3	17.9	17.1	89.5
1,3,5-Trimethylbenzene	24.0	22.1	22.5	13.8	22.9	21.1	17.6	105
sec-Butylbenzene	25.9	25.3	27.8	16.1	28.6	24.7	18.1	124
1,2,4-Trimethylbenzene	30.6	39.2	22.4	18.0	22.7	26.6	28.2	133
1,3-Dichlorobenzene	20.3	20.6	18.2	13.0	17.6	17.9	15.2	89.7
p-iso-Propyltoluene	21.6	22.1	21.6	16.0	22.8	20.8	11.8	104
1,4-Dichlorobenzene	18.1	21.2	20.0	13.2	17.4	18.0	15.3	90.0
1,2-Dichlorobenzene	18.4	22.5	22.5	15.2	19.9	19.7	13.9	96.6
n-Butylbenzene	13.1	20.3	19.5	10.8	18.7	16.5	23.1	82.4
1,2,4-Trichlorobenzene	14.5	14.9	15.7	8.8	12.3	13.3	18.8	66.2
Hexachlorobutadiene	17.6	22.5	21.6	13.2	21.6	19.3	18.2	96.3
1,2,3-Trichlorobenzene	14.9	15.9	16.5	11.9	13.9	14.6	11.3	73.1

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18  
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng)					Mean	RSD	Mean Rec
	1	2	3	4	5			
Vinyl chloride	33.4	31.0	30.9	29.7	28.6	30.8	5.2	154
Trichlorofluoromethane	37.7	20.8	20.0	21.8	20.5	24.1	28.2	121
1,1-Dichloroethene	21.7	33.5	39.8	30.2	32.5	31.6	18.5	158
Methylene chloride	20.9	19.4	18.7	18.3	18.4	19.1	5.1	95.7
trans-1,2-Dichloroethene	21.8	18.9	20.4	17.9	17.8	19.4	7.9	96.8
1,1-Dichloroethane	23.8	21.9	21.3	21.3	20.5	21.8	5.2	109
cis-1,2-Dichloroethene	21.6	18.8	18.5	18.2	18.2	19.0	6.7	95.2
Bromochloromethane	22.3	19.5	19.3	19.0	19.2	20.0	6.0	100
Chloroform	20.5	17.1	17.3	16.5	15.9	17.5	9.2	87.3
1,1,1-Trichloroethane	16.4	11.9	10.7	9.5	9.4	11.6	22.4	57.8
Carbon tetrachloride	13.1	11.3	13.0	11.8	11.2	12.1	6.7	60.5
Benzene	21.1	19.3	18.7	18.2	16.9	18.8	7.4	94.1
Trichloroethene	19.6	16.4	16.5	16.5	15.5	16.9	8.3	84.5
1,2-Dichloropropane	21.8	19.0	18.3	18.8	16.5	18.9	9.0	94.4
Dibromomethane	20.9	17.9	17.9	17.2	18.3	18.4	6.9	92.1
Bromodichloromethane	20.9	18.0	18.9	18.2	17.3	18.6	6.6	93.2
Toluene	22.2	17.3	18.8	17.0	15.9	18.2	12.0	91.2
1,1,2-Trichloroethane	21.0	16.5	17.2	17.2	16.5	17.7	9.6	88.4
1,3-Dichloropropane	21.4	17.3	18.7	18.6	16.7	18.5	8.8	92.6
Dibromochloromethane	20.9	18.1	19.0	18.8	16.6	18.7	7.5	93.3
Chlorobenzene	20.8	18.4	17.6	16.8	14.8	17.7	11.2	88.4
1,1,1,2-Tetrachloroethane	19.5	19.0	17.8	17.2	16.5	18.0	6.2	90.0
Ethylbenzene	21.1	18.3	18.5	16.9	15.3	18.0	10.6	90.0
p-Xylene	20.0	17.4	18.2	16.3	14.4	17.3	10.9	86.3
o-Xylene	20.7	17.2	16.8	16.2	14.8	17.1	11.4	85.7
Styrene	18.3	15.9	16.2	15.3	13.7	15.9	9.3	79.3
Bromoform	20.1	15.9	17.1	17.5	16.1	17.3	8.6	86.7
iso-Propylbenzene	21.0	18.1	19.2	18.4	15.6	18.4	9.6	92.2
Bromobenzene	20.4	16.2	17.2	16.7	15.4	17.2	10.1	85.9
1,1,2,2-Tetrachloroethane	23.3	17.9	21.2	18.8	16.8	19.6	12.1	96.0
1,2,3-Trichloropropane	18.4	14.6	15.6	16.1	15.6	16.1	8.0	80.3
n-Propylbenzene	20.4	18.9	17.9	17.0	14.3	17.7	11.6	88.4
2-Chlorotoluene	19.1	17.3	16.1	16.0	14.4	16.7	9.2	83.6
4-Chlorotoluene	19.0	15.5	16.8	15.9	13.6	16.4	10.6	81.8
1,3,5-Trimethylbenzene	20.8	18.0	17.4	16.1	14.7	17.4	11.7	86.9
sec-Butylbenzene	21.4	18.3	18.9	17.0	14.9	18.1	11.8	90.5
1,2,4-Trimethylbenzene	20.5	18.6	16.8	15.3	13.7	17.0	14.1	85.0
1,3-Dichlorobenzene	17.6	15.9	15.6	14.2	14.4	15.6	7.9	77.8
p-iso-Propyltoluene	20.5	17.0	17.1	15.6	13.4	16.7	13.9	83.6
1,4-Dichlorobenzene	18.5	13.8	14.8	16.7	14.9	15.7	10.5	78.7
1,2-Dichlorobenzene	18.4	15.0	15.4	15.3	13.5	15.5	10.5	77.6
n-Butylbenzene	19.6	15.9	15.9	14.4	18.9	16.9	11.7	84.6
1,2,4-Trichlorobenzene	15.2	17.2	17.4	13.6	12.1	15.1	13.5	75.4
Hexachlorobutadiene	18.7	16.2	15.5	13.8	16.6	16.1	10.0	80.7
Naphthalene	13.9	11.1	10.2	10.8	11.4	11.5	11.0	57.4
1,2,3-Trichlorobenzene	14.9	15.2	16.8	13.7	12.7	14.7	9.5	73.2

TABLE 19  
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng)					Mean	RSD	Mean Rec
	1	2	3	4	5			
Vinyl chloride	12.7	10.9	9.8	8.1	7.2	9.7	20.2	48.7
Trichlorofluoromethane	33.7	6.4	30.3	27.8	22.9	24.2	39.6	121
1,1-Dichloroethene	27.7	20.5	24.1	15.1	13.2	20.1	26.9	101
Methylene chloride	25.4	23.9	24.7	22.2	24.2	24.1	4.4	120
trans-1,2-Dichloroethene	2.8	3.0	3.3	2.2	2.4	2.7	15.0	13.6
1,1-Dichloroethane	24.1	26.3	27.0	20.5	21.2	23.8	11.0	119
cis-1,2-Dichloroethene	8.3	10.2	8.7	5.8	6.4	7.9	20.1	39.4
Bromochloromethane	11.1	11.8	10.2	8.8	9.0	10.2	11.2	50.9
Chloroform	16.7	16.9	17.0	13.8	15.0	15.9	7.9	79.3
1,1,1-Trichloroethane	24.6	22.8	22.1	16.2	20.9	21.3	13.4	107
Carbon tetrachloride	19.4	20.3	22.2	20.0	20.2	20.4	4.6	102
Benzene	21.4	22.0	22.4	19.6	20.4	21.2	4.9	106
Trichloroethene	12.4	16.5	14.9	9.0	9.9	12.5	22.9	62.7
1,2-Dichloropropane	19.0	18.8	19.7	16.0	17.6	18.2	7.1	91.0
Dibromomethane	7.3	8.0	6.9	5.6	6.8	6.9	11.3	34.6
Bromodichloromethane	14.9	15.9	15.9	12.8	13.9	14.7	8.3	73.3
Toluene	42.6	39.3	45.1	39.9	45.3	42.4	5.9	212
1,1,2-Trichloroethane	13.9	15.2	1.4	21.3	14.9	15.9	17.0	79.6
1,3-Dichloropropane	13.3	16.7	11.3	10.9	9.5	12.3	20.3	61.7
Dibromochloromethane	14.5	13.1	14.5	11.9	14.4	13.7	7.6	68.3
Chlorobenzene	8.4	10.0	8.3	6.9	7.8	8.3	12.1	41.3
1,1,1,2-Tetrachloroethane	16.7	16.7	15.6	15.8	15.7	16.1	3.2	80.4
Ethylbenzene	22.1	21.4	23.1	20.1	22.6	21.9	4.8	109
p-Xylene	41.4	38.4	43.8	38.3	44.0	41.2	6.1	206
o-Xylene	31.7	30.8	34.3	30.4	33.2	32.1	4.6	160
Styrene	0	0	0	0	0	0	0	0
Bromoform	8.6	8.9	9.1	7.0	7.7	8.3	9.4	41.4
iso-Propylbenzene	18.1	18.8	9.7	18.3	19.6	18.9	3.5	94.4
Bromobenzene	5.1	5.4	5.3	4.4	4.0	4.8	11.6	24.1
1,1,2,2-Tetrachloroethane	14.0	13.5	14.7	15.3	17.1	14.9	8.5	74.5
1,2,3-Trichloropropane	11.0	12.7	11.7	11.7	11.9	11.8	4.5	59.0
n-Propylbenzene	13.4	13.3	14.7	12.8	13.9	13.6	4.7	68.1
2-Chlorotoluene	8.3	9.0	11.7	8.7	7.9	9.1	14.8	45.6
4-Chlorotoluene	5.1	5.4	5.5	4.8	4.5	5.0	7.9	25.2
1,3,5-Trimethylbenzene	31.3	27.5	33.0	31.1	33.6	31.3	6.8	157
sec-Butylbenzene	13.5	13.4	16.4	13.8	15.4	14.5	8.3	72.5
1,2,4-Trimethylbenzene	38.7	32.4	40.8	34.1	40.3	37.3	9.1	186
1,3-Dichlorobenzene	3.6	3.6	3.7	3.0	3.2	3.4	8.0	17.2
p-iso-Propyltoluene	14.7	14.1	16.1	13.9	15.1	14.8	5.2	73.8
1,4-Dichlorobenzene	3.0	3.5	3.3	2.6	2.8	3.0	10.2	15.0
1,2-Dichlorobenzene	3.6	4.3	4.0	3.5	3.6	3.8	8.3	19.0
n-Butylbenzene	17.4	13.8	14.0	18.9	24.0	17.6	21.2	88.0
1,2,4-Trichlorobenzene	2.8	2.9	3.3	2.6	3.2	3.0	8.5	15.0
Hexachlorobutadiene	4.8	4.0	6.1	5.6	6.0	5.3	15.1	26.4
Naphthalene	5.5	5.1	5.5	4.7	5.6	5.3	6.2	26.5
1,2,3-Trichlorobenzene	2.2	2.3	2.4	2.2	2.3	2.3	3.5	11.4

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL  
USING VACUUM DISTILLATION (METHOD 5032)<sup>a</sup>

Compound	Soil/H <sub>2</sub> O <sup>b</sup> Recovery		Soil/Oil <sup>c</sup> Recovery		Soil/Oil/H <sub>2</sub> O Recovery	
	Mean	RSD	Mean	RSD	Mean	RSD
Chloromethane	61	20	40	18	108	68
Bromomethane	58	20	47	13	74	13
Vinyl chloride	54	12	46	11	72	20
Chloroethane	46	10	41	8	52	14
Methylene chloride	60	2	65	8	76	11
Acetone	INT <sup>e</sup>	INT	44	8		
Carbon disulfide	47	13	53	10	47	4
1,1-Dichloroethene	48	9	47	5	58	3
1,1-Dichloroethane	61	6	58	9	61	6
trans-1,2-Trichloroethane	54	7	60	7	56	5
cis-1,2-Dichloroethene	60	4	72	6	63	8
Chloroform	104	11	93	6	114	15
1,2-Dichloroethane	177	50	117	8	151	22
2-Butanone	INT	36	38	INT		
1,1,1-Trichloroethane	124	13	72	16	134	26
Carbon tetrachloride	172	122	INT	INT		
Vinyl acetate	88	11	INT			
Bromodichloromethane	93	4	91	23	104	23
1,1,2,2-Tetrachloroethane	96	13	50	12	104	7
1,2-Dichloropropane	105	8	102	6	111	6
trans-1,3-Dichloropropene	134	10	84	16	107	8
Trichloroethene	98	9	99	10	100	5
Dibromochloromethane	119	8	125	31	142	16
1,1,2-Trichloroethane	126	10	72	16	97	4
Benzene	99	7	CONT <sup>f</sup>	CONT		
cis-1,3-Dichloropropene	123	12	94	13	112	9
Bromoform	131	13	58	18	102	9
2-Hexanone	155	18	164	19	173	29
4-Methyl-2-pentanone	152	20	185	20	169	18
Tetrachloroethene	90	9	123	14	128	7
Toluene	94	3	CONT	CONT		
Chlorobenzene	98	7	93	18	112	5
Ethylbenzene	114	13	CONT	CONT		
Styrene	106	8	93	18	112	5
p-Xylene	97	9	CONT	CONT		
o-Xylene	105	8	112	12	144	13

TABLE 20 (cont.)

Compound	Soil/H <sub>2</sub> O <sup>b</sup> Recovery		Soil/Oil <sup>c</sup> Recovery		Soil/Oil/H <sub>2</sub> O Recovery	
	Mean	RSD	Mean	RSD	Mean	RSD
Surrogates						
1,2-Dichloroethane	177	50	117	8	151	22
Toluene-d <sub>8</sub>	96	6	79	12	82	6
Bromofluorobenzene	139	13	37	13	62	5

<sup>a</sup> Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

<sup>b</sup> Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

<sup>c</sup> Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

<sup>d</sup> Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

<sup>e</sup> Interference by co-eluting compounds prevented accurate measurement of analyte.

<sup>f</sup> Contamination of sample matrix by analyte prevented assessment of efficiency.



TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES  
IN FISH TISSUE (METHOD 5032)<sup>a</sup>

Compound	Efficiency	
	Mean (%)	RSD (%)
Chloromethane	N/A <sup>b</sup>	
Bromomethane	N/A <sup>b</sup>	
Vinyl chloride	N/A <sup>b</sup>	
Chloroethane	N/A <sup>b</sup>	
Methylene chloride	CONT <sup>c</sup>	
Acetone	CONT <sup>c</sup>	
Carbon disulfide	79	36
1,1-Dichloroethene	122	39
1,1-Dichloroethane	126	35
trans-1,2-Trichloroethene	109	46
cis-1,2-Dichloroethene	106	22
Chloroform	111	32
1,2-Dichloroethane	117	27
2-Butanone	INT <sup>d</sup>	
1,1,1-Trichloroethane	106	30
Carbon tetrachloride	83	34
Vinyl acetate	INT <sup>d</sup>	
Bromodichloromethane	97	22
1,1,2,2-Tetrachloroethane	67	20
1,2-Dichloropropane	117	23
trans-1,3-Dichloropropene	92	22
Trichloroethene	98	31
Dibromochloromethane	71	19
1,1,2-Trichloroethane	92	20
Benzene	129	35
cis-1,3-Dichloropropene	102	24
Bromoform	58	19
2-Hexanone	INT <sup>d</sup>	
4-Methyl-2-pentanone	113	37
Tetrachloroethene	66	20
Toluene	CONT <sup>c</sup>	
Chlorobenzene	65	19
Ethylbenzene	74	19
Styrene	57	14
p-Xylene	46	13
o-Xylene	83	20

TABLE 21 (cont.)

Compound	Efficiency	
	Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	115	27
Toluene-d <sub>8</sub>	88	24
Bromofluorobenzene	52	15

<sup>a</sup> Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

<sup>b</sup> No analyses.

<sup>c</sup> Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

<sup>d</sup> Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES  
IN FISH TISSUE (METHOD 5032)<sup>a</sup>

Compound	Method Detection Limit (ppb)	
	External Standard Method	Internal Standard Method
Chloromethane	7.8	7.3
Bromomethane	9.7	9.8
Vinyl chloride	9.5	9.4
Chloroethane	9.2	10.0
Methylene chloride	CONT <sup>b</sup>	CONT <sup>b</sup>
Acetone	CONT <sup>b</sup>	CONT <sup>b</sup>
Carbon disulfide	5.4	4.9
1,1-Dichloroethene	4.0	5.7
1,1-Dichloroethane	4.0	3.5
trans-1,2-Dichloroethene	4.4	4.0
cis-1,2-Dichloroethene	4.7	4.1
Chloroform	5.6	5.0
1,2-Dichloroethane	3.3	3.2
2-Butanone	INT <sup>c</sup>	INT <sup>c</sup>
1,1,1-Trichloroethane	1.1	4.2
Carbon tetrachloride	3.2	3.5
Vinyl acetate	INT <sup>c</sup>	INT <sup>c</sup>
Bromodichloromethane	3.2	2.8
1,1,2,2-Tetrachloroethane	4.4	3.8
1,2-Dichloropropane	3.8	3.7
trans-1,3-Dichloropropene	3.4	3.0
Trichloroethene	3.1	4.0
Dibromochloromethane	3.5	3.2
1,1,2-Trichloroethane	4.4	3.3
Benzene	3.6	3.2
cis-1,3-Dichloropropene	3.5	3.0
Bromoform	4.9	4.0
2-Hexanone	7.7	8.0
4-Methyl-2-pentanone	7.5	8.0
Tetrachloroethene	4.3	4.0
Toluene	3.0	2.5
Chlorobenzene	3.3	2.8
Ethylbenzene	3.6	3.5
Styrene	3.5	3.3
p-Xylene	3.7	3.5
o-Xylene	3.3	4.7

Footnotes are on the following page.

TABLE 22 (cont.)

---

- <sup>a</sup> Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.
- <sup>b</sup> Contamination of sample by analyte prevented determination.
- <sup>c</sup> Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER  
USING VACUUM DISTILLATION (METHOD 5032)<sup>a</sup>

Compound	5 mL H <sub>2</sub> O <sup>b</sup> Recovery		20 mL H <sub>2</sub> O <sup>c</sup> Recovery		20 mL H <sub>2</sub> O/Oil Recovery	
	Mean	RSD	Mean	RSD	Mean	RSD
Chloromethane	114	27	116	29	176	67
Bromomethane	131	14	121	14	113	21
Vinyl chloride	131	13	120	16	116	23
Chloroethane	110	15	99	8	96	16
Methylene chloride	87	16	105	15	77	6
Acetone	83	22	65	34	119	68
Carbon disulfide	138	17	133	23	99	47
1,1-Dichloroethene	105	11	89	4	96	18
1,1-Dichloroethane	118	10	119	11	103	25
trans-1,2-Dichloroethene	105	11	107	14	96	18
cis-1,2-Dichloroethene	106	7	99	5	104	23
Chloroform	114	6	104	8	107	21
1,2-Dichloroethane	104	6	109	8	144	19
2-Butanone	83	50	106	31	INT <sup>c</sup>	
1,1,1-Trichloroethane	118	9	109	9	113	23
Carbon tetrachloride	102	6	108	12	109	27
Vinyl acetate	90	16	99	7	72	36
Bromodichloromethane	104	3	110	5	99	5
1,1,2,2-Tetrachloroethane	85	17	81	7	111	43
1,2-Dichloropropane	100	6	103	2	104	7
trans-1,3-Dichloropropene	105	8	105	4	92	4
Trichloroethene	98	4	99	2	95	5
Dibromochloroethane	99	8	99	6	90	25
1,1,2-Trichloroethane	98	7	100	4	76	12
Benzene	97	4	100	5	112	10
cis-1,3-Dichloropropene	106	5	105	4	98	3
Bromoform	93	16	94	8	57	21
2-Hexanone	60	17	63	16	78	23
4-Methyl-2-pentanone	79	24	63	14	68	15
Tetrachloroethene	101	3	97	7	77	14
Toluene	100	6	97	8	85	5
Chlorobenzene	98	6	98	4	88	16
Ethylbenzene	100	3	92	8	73	13
Styrene	98	4	97	9	88	16
p-Xylene	96	4	94	8	60	12
o-Xylene	96	7	95	6	72	14

TABLE 23 (cont.)

Compound	5 mL H <sub>2</sub> O <sup>b</sup> Recovery		20 mL H <sub>2</sub> O <sup>c</sup> Recovery		20 mL H <sub>2</sub> O/Oil Recovery	
	Mean	RSD	Mean	RSD	Mean	RSD
Surrogates						
1,2-Dichloroethane	104	6	109	6	144	19
Toluene-d <sub>8</sub>	104	5	102	2	76	7
Bromofluorobenzene	106	6	106	9	40	8

<sup>a</sup> Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

<sup>b</sup> Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

<sup>c</sup> Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES  
USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)<sup>a</sup>

Compound	Water <sup>b</sup> (µg/L)	Soil <sup>c</sup> (µg/kg)	Tissue <sup>d</sup> (µg/kg)	Oil <sup>e</sup> (mg/kg)
Chloromethane	3.2	8.0	7.3	N/A <sup>f</sup>
Bromomethane	2.8	4.9	9.8	N/A <sup>f</sup>
Vinyl chloride	3.5	6.0	9.4	N/A <sup>f</sup>
Chloroethane	5.9	6.0	10.0	N/A <sup>f</sup>
Methylene chloride	3.1	4.0	CONT <sup>g</sup>	0.05
Acetone	5.6	CONT <sup>g</sup>	CONT <sup>g</sup>	0.06
Carbon disulfide	2.5	2.0	4.9	0.18
1,1-Dichloroethene	2.9	3.2	5.7	0.18
1,1-Dichloroethane	2.2	2.0	3.5	0.14
trans-1,2-Dichloroethene	2.2	1.4	4.0	0.10
cis-1,2-Dichloroethene	2.0	2.3	4.1	0.07
Chloroform	2.4	1.8	5.0	0.07
1,2-Dichloroethane	1.7	1.5	3.2	0.06
2-Butanone	7.4	INT <sup>h</sup>	INT <sup>h</sup>	INT <sup>h</sup>
1,1,1-Trichloroethane	1.8	1.7	4.2	0.10
Carbon tetrachloride	1.4	1.5	3.5	0.13
Vinyl acetate	11.8	INT <sup>h</sup>	INT <sup>h</sup>	INT <sup>h</sup>
Bromodichloromethane	1.6	1.4	2.8	0.06
1,1,2,2-Tetrachloroethane	2.5	2.1	3.8	0.02
1,2-Dichloropropane	2.2	2.1	3.7	0.15
trans-1,3-Dichloropropene	1.5	1.7	3.0	0.05
Trichloroethene	1.6	1.7	4.0	0.04
Dibromochloromethane	1.7	1.5	3.2	0.07
1,1,2-Trichloroethane	2.1	1.7	3.3	0.05
Benzene	0.5	1.5	3.2	0.05
cis-1,3-Dichloropropene	1.4	1.7	3.0	0.04
Bromoform	1.8	1.5	4.0	0.05
2-Hexanone	4.6	3.6	8.0	INT <sup>h</sup>
4-Methyl-2-pentanone	3.5	4.6	8.0	INT <sup>h</sup>
Tetrachloroethene	1.4	1.6	4.0	0.10
Toluene	1.0	3.3	2.5	0.05
Chlorobenzene	1.4	1.4	2.8	0.06
Ethylbenzene	1.5	2.8	3.5	0.04
Styrene	1.4	1.4	3.3	0.18
p-Xylene	1.5	2.9	3.5	0.20
o-Xylene	1.7	3.4	4.7	0.07

Footnotes are found on the following page.

TABLE 24 (cont.)

- 
- a Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1  $\mu$ m film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.
- b Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.
- c Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1  $\mu$ m film thickness.
- d Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.
- e No analyses.
- f Contamination of sample by analyte prevented determination.
- g Interference by co-eluting compounds prevented accurate quantitation.



TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES  
(METHOD 5032) (EXTERNAL STANDARD METHOD)<sup>a</sup>

Compound	Water <sup>b</sup> (µg/L)	Soil <sup>c</sup> (µg/kg)	Tissue <sup>d</sup> (µg/kg)	Oil <sup>e</sup> (mg/kg)
Chloromethane	3.1	8.6 <sup>f</sup>	7.8	N/A <sup>g</sup>
Bromomethane	2.5	4.9 <sup>f</sup>	9.7	N/A <sup>g</sup>
Vinyl chloride	4.0	7.1 <sup>f</sup>	9.5	N/A <sup>g</sup>
Chloroethane	6.1	7.5 <sup>f</sup>	9.2	N/A <sup>g</sup>
Methylene chloride	3.1	3.3	CONT <sup>h</sup>	0.08
Acetone	33.0 <sup>f</sup>	CONT <sup>h</sup>	CONT <sup>h</sup>	0.12
Carbon disulfide	2.5	3.2	5.4	0.19
1,1-Dichloroethene	3.4	3.8	4.0	0.19
1,1-Dichloroethane	2.3	1.7	4.0	0.13
trans-1,2-Dichloroethene	3.0	3.2	4.4	0.09
cis-1,2-Dichloroethene	2.4	2.7	4.7	0.08
Chloroform	2.7	2.6	5.6	0.06
1,2-Dichloroethane	1.6	1.7	3.3	0.06
2-Butanone	57.0 <sup>f</sup>	INT <sup>i</sup>	INT <sup>i</sup>	INT <sup>i</sup>
1,1,1-Trichloroethane	1.6	2.4	1.1	0.08
Carbon tetrachloride	1.5	1.7	3.2	0.15
Vinyl acetate	23.0 <sup>f</sup>	INT <sup>i</sup>	INT <sup>i</sup>	INT <sup>i</sup>
Bromodichloromethane	2.0	2.3	3.2	0.05
1,1,2,2-Tetrachloroethane	3.6	3.2	4.4	0.09
1,2-Dichloropropane	2.9	3.7	3.8	0.12
trans-1,3-Dichloropropene	2.3	2.4	3.8	0.08
Trichloroethene	2.5	3.0	3.1	0.06
Dibromochloromethane	2.1	2.9	3.5	0.04
1,1,2-Trichloroethane	2.7	2.8	4.4	0.07
Benzene	1.7	2.9	3.6	0.03
cis-1,3-Dichloropropene	2.1	2.5	3.5	0.06
Bromoform	2.3	2.5	4.9	0.10
2-Hexanone	4.6	4.6	7.7	INT <sup>i</sup>
4-Methyl-2-pentanone	3.8	3.9	7.5	INT <sup>i</sup>
Tetrachloroethene	1.8	2.6	4.3	0.12
Toluene	1.8	4.4	3.0	0.09
Chlorobenzene	2.4	2.6	3.3	0.07
Ethylbenzene	2.4	4.1	3.6	0.09
Styrene	2.0	2.5	3.5	0.16
p-Xylene	2.3	3.9	3.7	0.18
o-Xylene	2.4	4.1	3.3	0.08

TABLE 25 (cont.)

- 
- <sup>a</sup> Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.
- <sup>b</sup> Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.
- <sup>c</sup> These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.
- <sup>d</sup> These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.
- <sup>e</sup> Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.
- <sup>f</sup> Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.
- <sup>g</sup> No analyses.
- <sup>h</sup> Contamination of sample by analyte prevented determination.
- <sup>i</sup> Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL  
USING VACUUM DISTILLATION (METHOD 5032)<sup>a</sup>

Compound	Recovery	
	Mean (%)	RSD (%)
Chloromethane	N/A <sup>b</sup>	
Bromomethane	N/A <sup>b</sup>	
Vinyl chloride	N/A <sup>b</sup>	
Chloroethane	N/A <sup>b</sup>	
Methylene chloride	62	32
Acetone	108	55
Carbon disulfide	98	46
1,1-Dichloroethene	97	24
1,1-Dichloroethane	96	22
trans-1,2-Trichloroethene	86	23
cis-1,2-Dichloroethene	99	11
Chloroform	93	14
1,2-Dichloroethane	138	31
2-Butanone	INT <sup>c</sup>	
1,1,1-Trichloroethane	89	14
Carbon tetrachloride	129	23
Vinyl acetate	INT <sup>c</sup>	
Bromodichloromethane	106	14
1,1,2,2-Tetrachloroethane	205	46
1,2-Dichloropropane	107	24
trans-1,3-Dichloropropene	98	13
Trichloroethene	102	8
Dibromochloromethane	168	21
1,1,2-Trichloroethane	95	7
Benzene	146	10
cis-1,3-Dichloropropene	98	11
Bromoform	94	18
2-Hexanone	INT <sup>c</sup>	
4-Methyl-2-pentanone	INT <sup>c</sup>	
Tetrachloroethene	117	22
Toluene	108	8
Chlorobenzene	101	12
Ethylbenzene	96	10
Styrene	120	46
p-Xylene	87	23
o-Xylene	90	10

TABLE 26 (cont.)

Compound	Recovery	
	Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	137	30
Toluene-d <sub>8</sub>	84	6
Bromofluorobenzene	48	2

<sup>a</sup> Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

<sup>b</sup> Not analyzed.

<sup>c</sup> Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES  
IN OIL (METHOD 5032)<sup>a</sup>

Compound	Method Detection Limit (ppb)	
	External Standard Method	Internal Standard Method
Chloromethane	N/A <sup>b</sup>	N/A <sup>b</sup>
Bromomethane	N/A <sup>b</sup>	N/A <sup>b</sup>
Vinyl chloride	N/A <sup>b</sup>	N/A <sup>b</sup>
Chloroethane	N/A <sup>b</sup>	N/A <sup>b</sup>
Methylene chloride	80	50
Acetone	120	60
Carbon disulfide	190	180
1,1-Dichloroethene	190	180
1,1-Dichloroethane	130	140
trans-1,2-Dichloroethene	90	100
cis-1,2-Dichloroethene	80	70
Chloroform	60	70
1,2-Dichloroethane	60	60
2-Butanone	INT <sup>c</sup>	INT <sup>c</sup>
1,1,1-Trichloroethane	80	100
Carbon tetrachloride	150	130
Vinyl acetate	INT <sup>c</sup>	INT <sup>c</sup>
Bromodichloromethane	50	60
1,1,2,2-Tetrachloroethane	90	20
1,2-Dichloropropane	120	150
trans-1,3-Dichloropropene	80	50
Trichloroethene	60	40
Dibromochloromethane	40	70
1,1,2-Trichloroethane	70	50
Benzene	30	50
cis-1,3-Dichloropropene	60	40
Bromoform	100	50
2-Hexanone	INT <sup>c</sup>	INT <sup>c</sup>
4-Methyl-2-pentanone	INT <sup>c</sup>	INT <sup>c</sup>
Tetrachloroethene	120	100
Toluene	90	50
Chlorobenzene	70	60
Ethylbenzene	90	40
Styrene	160	180
p-Xylene	180	200
o-Xylene	80	70

TABLE 27 (cont.)

- 
- <sup>a</sup> Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.
- <sup>b</sup> No analyses.
- <sup>c</sup> Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS  
(METHOD 5021)

Chloroform-d <sub>1</sub>	1,1,2-TCA-d <sub>3</sub>	Bromobenzene-d <sub>5</sub>
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Chloromethane	1,1-Dichloropropene	Bromoform
Vinyl chloride	Carbon tetrachloride	Styrene
Bromomethane	Benzene	iso-Propylbenzene
Chloroethane	Dibromomethane	Bromobenzene
Trichlorofluoromethane	1,2-Dichloropropane	n-Propylbenzene
1,1-Dichloroethene	Trichloroethene	2-Chlorotoluene
Methylene chloride	Bromodichloromethane	4-Chlorotoluene
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
1,1-Dichloroethane	trans-1,3-Dichloropropene	tert-Butylbenzene
cis-1,2-Dichloroethene	1,1,2-Trichloroethane	1,2,4-Trimethylbenzene
Bromochloromethane	Toluene	sec-Butylbenzene
Chloroform	1,3-Dichloropropane	1,3-Dichlorobenzene
2,2-Dichloropropane	Dibromochloromethane	1,4-Dichlorobenzene
1,2-Dichloroethane	1,2-Dibromoethane	p-iso-Propyltoluene
	Tetrachloroethene	1,2-Dichlorobenzene
	1,1,2-Trichloroethane	n-Butylbenzene
	Ethylbenzene	1,2-Dibromo-3-chloropropane
	m-Xylene	1,2,4-Trichlorobenzene
	p-Xylene	Naphthalene
	o-Xylene	Hexachlorobutadiene
	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
	1,2,3-Trichloropropane	

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND<sup>a</sup> (METHOD 5021)

Compound	% RSD	MDL (µg/kg)
Benzene	3.0	0.34
Bromochloromethane	3.4	0.27
Bromodichloromethane	2.4	0.21
Bromoform	3.9	0.30
Bromomethane	11.6	1.3
Carbon tetrachloride	3.6	0.32
Chlorobenzene	3.2	0.24
Chloroethane	5.6	0.51
Chloroform	3.1	0.30
Chloromethane	4.1	3.5 <sup>b</sup>
1,2-Dibromo-3-chloropropane	5.7	0.40
1,2-Dibromoethane	3.2	0.29
Dibromomethane	2.8	0.20
1,2-Dichlorobenzene	3.3	0.27
1,3-Dichlorobenzene	3.4	0.24
1,4-Dichlorobenzene	3.7	0.30
Dichlorodifluoromethane	3.0	0.28
1,1-Dichloroethane	4.5	0.41
1,2-Dichloroethane	3.0	0.24
1,1-Dichloroethene	3.3	0.28
cis-1,2-Dichloroethene	3.2	0.27
trans-1,2-Dichloroethene	2.6	0.22
1,2-Dichloropropane	2.6	0.21
1,1-Dichloropropene	3.2	0.30
cis-1,3-Dichloropropene	3.4	0.27
Ethylbenzene	4.8	0.47
Hexachlorobutadiene	4.1	0.38
Methylene chloride	8.2	0.62 <sup>c</sup>
Naphthalene	16.8	3.4 <sup>c</sup>
Styrene	7.9	0.62
1,1,1,2-Tetrachloroethane	3.6	0.27
1,1,2,2-Tetrachloroethane	2.6	0.20
Tetrachloroethene	9.8	1.2 <sup>c</sup>
Toluene	3.5	0.38
1,2,4-Trichlorobenzene	4.2	0.44
1,1,1-Trichloroethane	2.7	0.27
1,1,2-Trichloroethane	2.6	0.20
Trichloroethene	2.3	0.19



TABLE 29 (cont.)

Compound	% RSD	MDL (µg/kg)
Trichlorofluoromethane	2.7	0.31
1,2,3-Trichloropropane	1.5	0.11
Vinyl chloride	4.8	0.45
m-Xylene/p-Xylene	3.6	0.37
o-Xylene	3.6	0.33

<sup>a</sup> Most compounds spiked at 2 ng/g (2 µg/kg)

<sup>b</sup> Incorrect ionization due to methanol

<sup>c</sup> Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

Compound	Recovery per Replicate (ng)			Mean (ng)	RSD	Recovery (%)
	Sample 1	Sample 2	Sample 3			
Benzene	37.6	35.2	38.4	37.1	3.7	185 <sup>a</sup>
Bromochloromethane	20.5	19.4	20.0	20.0	2.3	100
Bromodichloromethane	21.1	20.3	22.8	21.4	4.9	107
Bromoform	23.8	23.9	25.1	24.3	2.4	121
Bromomethane	21.4	19.5	19.7	20.2	4.2	101
Carbon tetrachloride	27.5	26.6	28.6	27.6	3.0	138
Chlorobenzene	25.6	25.4	26.4	25.8	1.7	129
Chloroethane	25.0	24.4	25.3	24.9	1.5	125
Chloroform	21.9	20.9	21.7	21.5	2.0	108
Chloromethane	21.0	19.9	21.3	20.7	2.9	104 <sup>a</sup>
1,2-Dibromo-3-chloro- propane	20.8	20.8	21.0	20.9	0.5	104
1,2-Dibromoethane	20.1	19.5	20.6	20.1	2.2	100
Dibromomethane	22.2	21.0	22.8	22.0	3.4	110
1,2-Dichlorobenzene	18.0	17.7	17.1	17.6	2.1	88.0
1,3-Dichlorobenzene	21.2	21.0	20.1	20.8	2.3	104
1,4-Dichlorobenzene	20.1	20.9	19.9	20.3	2.1	102
Dichlorodifluoromethane	25.3	24.1	25.4	24.9	2.4	125
1,1-Dichloroethane	23.0	22.0	22.7	22.6	1.9	113
1,2-Dichloroethane	20.6	19.5	19.8	20.0	2.3	100
1,1-Dichloroethene	24.8	23.8	24.4	24.3	1.7	122
cis-1,2-Dichloroethene	21.6	20.0	21.6	21.1	3.6	105
trans-1,2-Dichloroethene	22.4	21.4	22.2	22.0	2.0	110
1,2-Dichloropropane	22.8	22.2	23.4	22.8	2.1	114
1,1-Dichloropropene	26.3	25.7	28.0	26.7	3.7	133
cis-1,3-Dichloropropene	20.3	19.5	21.1	20.3	3.2	102
Ethylbenzene	24.7	24.5	25.5	24.9	1.7	125
Hexachlorobutadiene	23.0	25.3	25.2	24.5	4.3	123
Methylene chloride	26.0	25.7	26.1	25.9	0.7	130 <sup>a</sup>
Naphthalene	13.8	12.7	11.8	12.8	6.4	63.8 <sup>a</sup>
Styrene	24.2	23.3	23.3	23.6	1.8	118
1,1,1,2-Tetrachloroethane	21.4	20.2	21.3	21.0	2.6	105
1,1,2,2-Tetrachloroethane	18.6	17.8	19.0	18.5	2.7	92.3
Tetrachloroethene	25.2	24.8	26.4	25.5	2.7	127
Toluene	28.6	27.9	30.9	29.1	4.4	146 <sup>a</sup>
1,2,4-Trichlorobenzene	15.0	14.4	12.9	14.1	6.3	70.5
1,1,1-Trichloroethane	28.1	27.2	29.9	28.4	4.0	142
1,1,2-Trichloroethane	20.8	19.6	21.7	20.7	4.2	104

TABLE 30 (cont.)

Compound	Recovery per Replicate (ng)			Mean (ng)	RSD	Recovery (%)
	Sample 1	Sample 2	Sample 3			
Trichloroethene	26.3	24.9	26.8	26.0	3.1	130
Trichlorofluoromethane	25.9	24.8	26.5	25.7	2.7	129
1,2,3-Trichloropropane	18.8	18.3	19.3	18.8	2.2	94.0
Vinyl chloride	24.8	23.2	23.9	24.0	2.7	120
m-Xylene/p-Xylene	24.3	23.9	25.3	24.5	2.4	123
o-Xylene	23.1	22.3	23.4	22.9	2.0	115

<sup>a</sup> Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS  
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)<sup>a</sup>

Compound	Detection Limit (ng)	Boiling Point (°C)
Chloromethane	58	-24
Bromomethane	26	4
Vinyl chloride	14	-13
Chloroethane	21	13
Methylene chloride	9	40
Acetone	35	56
Carbon disulfide	11	46
1,1-Dichloroethene	14	32
1,1-Dichloroethane	12	57
trans-1,2-Dichloroethene	11	48
Chloroform	11	62
1,2-Dichloroethane	13	83
1,1,1-Trichloroethane	8	74
Carbon tetrachloride	8	77
Bromodichloromethane	11	88
1,1,2,2-Tetrachloroethane**	23	146
1,2-Dichloropropane	12	95
trans-1,3-Dichloropropene	17	112
Trichloroethene	11	87
Dibromochloromethane	21	122
1,1,2-Trichloroethane	26	114
Benzene	26	80
cis-1,3-Dichloropropene	27	112
Bromoform**	26	150
Tetrachloroethene	11	121
Toluene	15	111
Chlorobenzene	15	132
Ethylbenzene**	21	136
Styrene**	46	145
Trichlorofluoromethane	17	24
Iodomethane	9	43
Acrylonitrile	13	78
Dibromomethane	14	97
1,2,3-Trichloropropane**	37	157
total Xylenes**	22	138-144

Footnotes are found on the following page.

TABLE 31 (cont.)

- 
- \* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.
- \*\* Boiling Point greater than 130°C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES  
ASSIGNED FOR QUANTITATION (METHOD 5041)

Bromochloromethane

Acetone  
Acrylonitrile  
Bromomethane  
Carbon disulfide  
Chloroethane  
Chloroform  
Chloromethane  
1,1-Dichloroethane  
1,2-Dichloroethane  
1,2-Dichloroethane-d<sub>4</sub> (surrogate)  
1,1-Dichloroethene  
Trichloroethene  
trans-1,2-Dichloroethene  
Iodomethane  
Methylene chloride  
Trichlorofluoromethane  
Vinyl chloride

Chlorobenzene-d<sub>5</sub>

4-Bromofluorobenzene (surrogate)  
Chlorobenzene  
Ethylbenzene  
Styrene  
1,1,2,2-Tetrachloroethane  
Tetrachloroethene  
Toluene  
Toluene-d<sub>8</sub> (surrogate)  
1,2,3-Trichloropropane  
Xylenes

1,4-Difluorobenzene

Benzene  
Bromodichloromethane  
Bromoform  
Carbon tetrachloride  
Chlorodibromomethane  
Dibromomethane  
1,2-Dichloropropane  
cis-1,3-Dichloropropene  
trans-1,3-Dichloropropene  
1,1,1-Trichloroethane  
1,1,2-Trichloroethane

TABLE 33

## METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

Compound	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Detection Limit <sup>a</sup> (ppm)
Dichlorodifluoromethane	-30	Gas	0.20
Vinyl chloride	-19	Gas	0.11
1,3-Butadiene	-4	Gas	0.90
1,2-Dichloro-1,1,2,2-tetrafluoroethane	4	Gas	0.14
Methyl bromide	4	Gas	0.14
Trichlorofluoromethane	24	88	0.18
1,1-Dichloroethene	31	22	0.07
Methylene chloride	40	44	0.05
1,1,2-Trichloro-trifluoroethane	48	37	0.13
Chloroform	61	21	0.04
1,1,1-Trichloroethane	75	13	0.03
Carbon tetrachloride	77	11	0.03
Benzene	80	10	0.16
Trichloroethene	87	8	0.04
1,2-Dichloropropane	96	5	0.05
Toluene	111	3	0.08
Tetrachloroethene	121	2	0.03

<sup>a</sup> Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1  
GAS CHROMATOGRAM OF VOLATILE ORGANICS

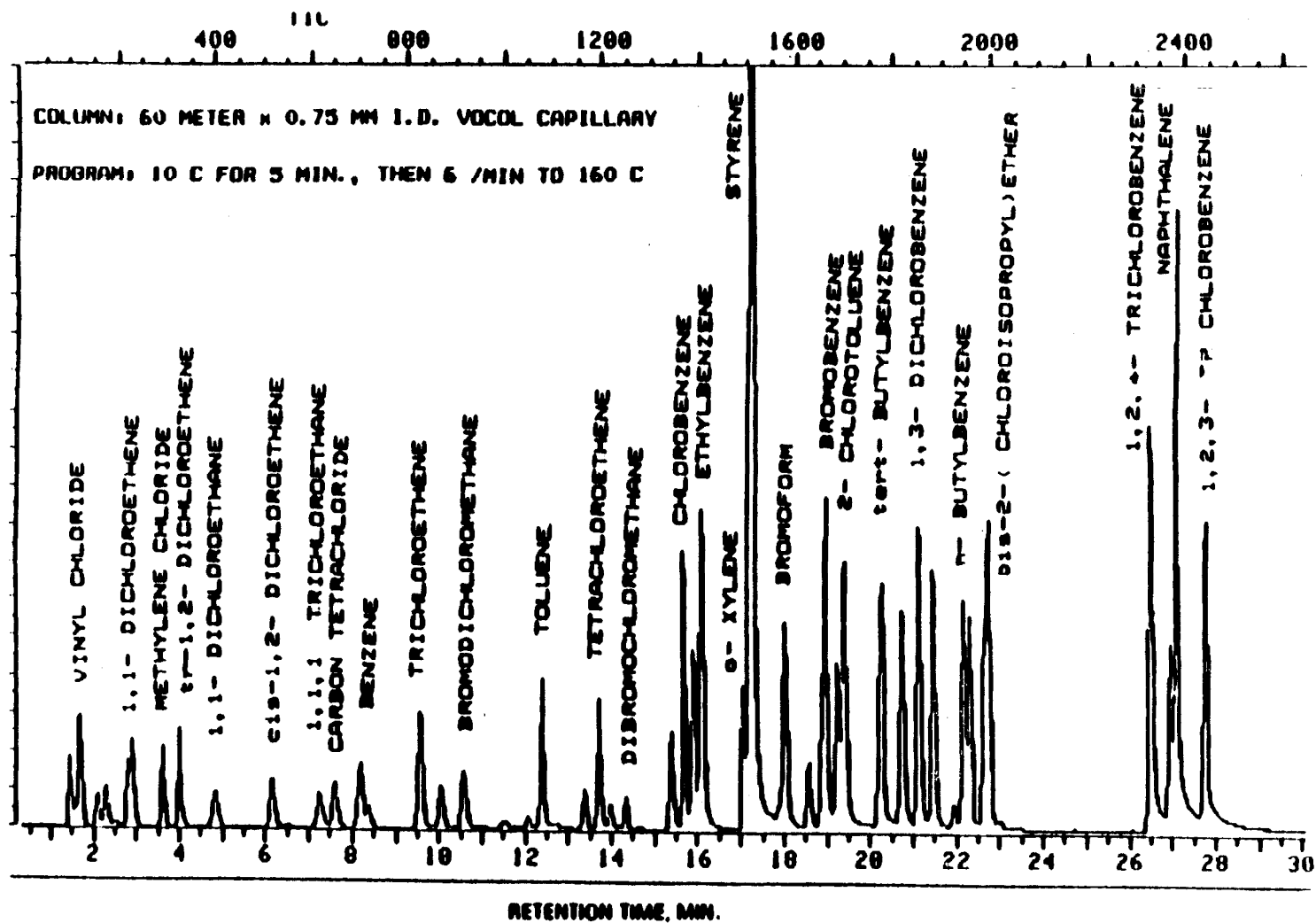




FIGURE 2  
GAS CHROMATOGRAM OF VOLATILE ORGANICS

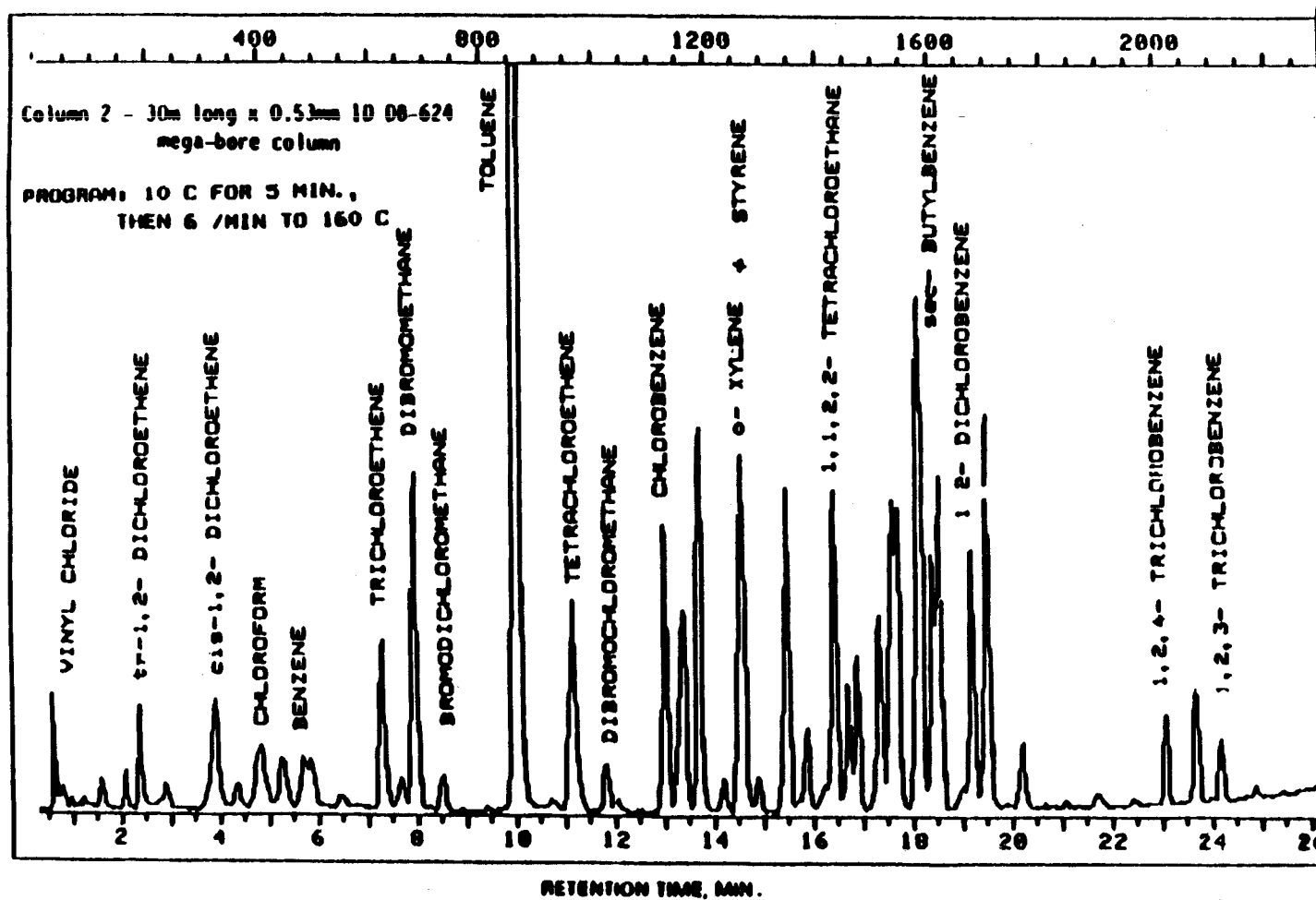
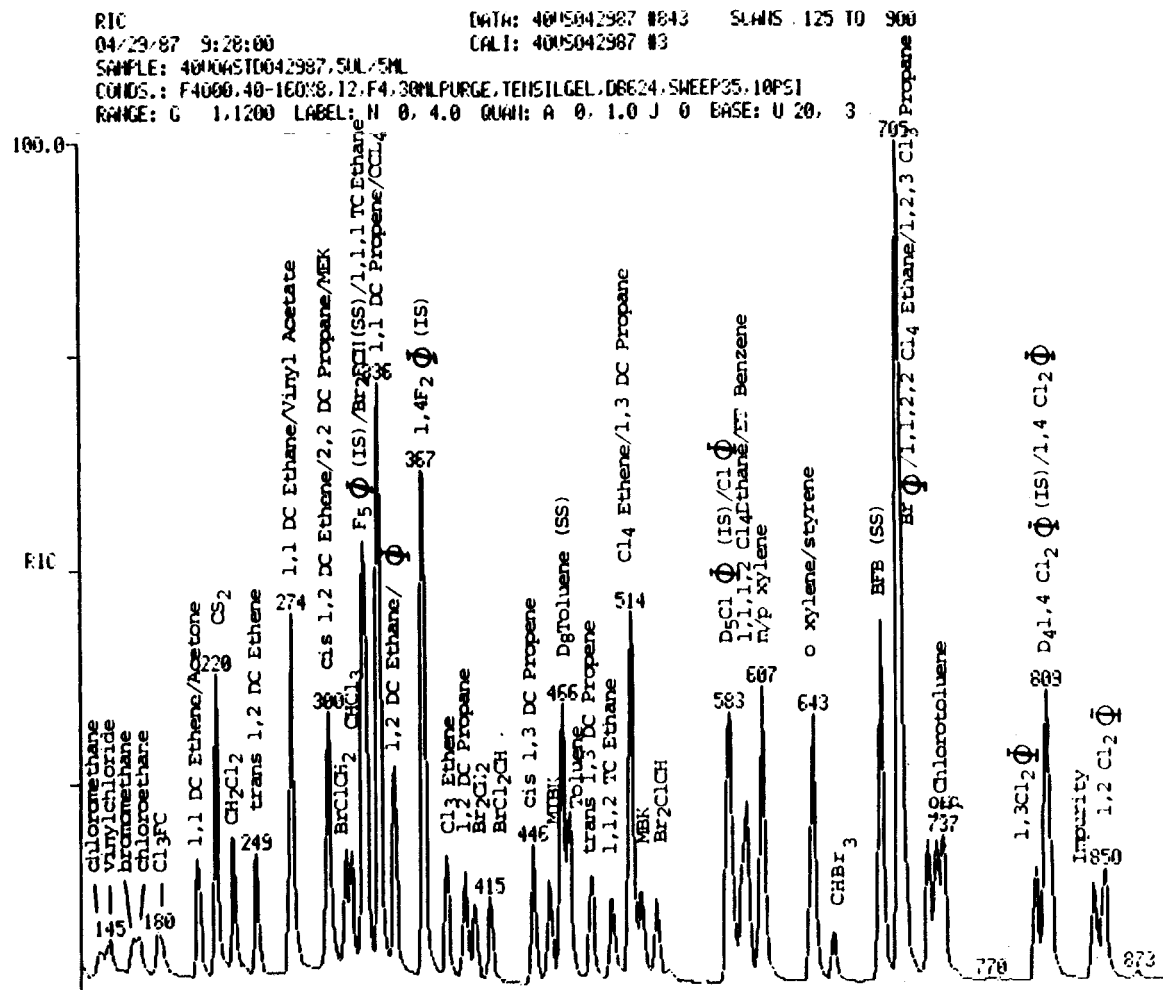
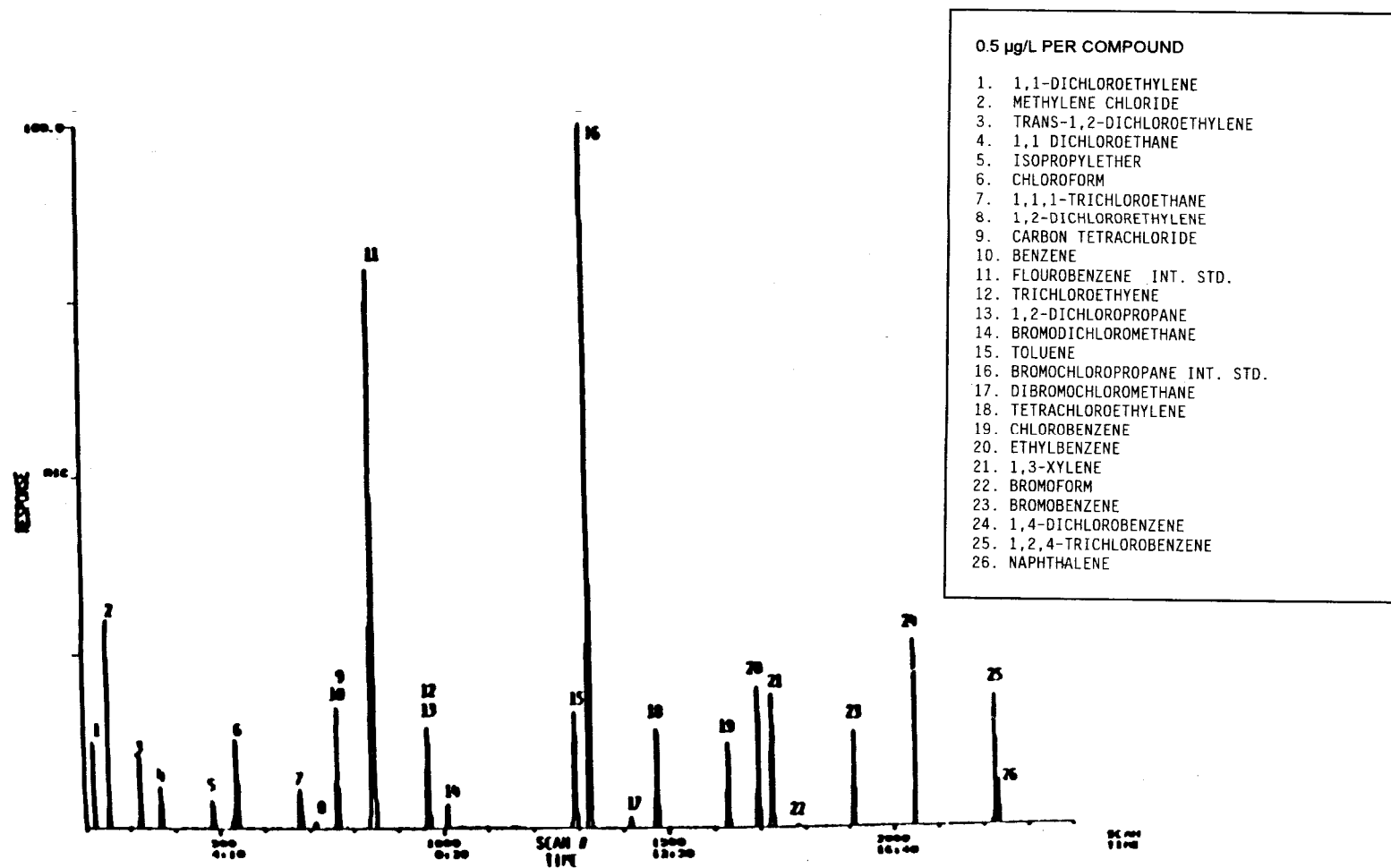


FIGURE 3  
GAS CHROMATOGRAM OF VOLATILE ORGANICS

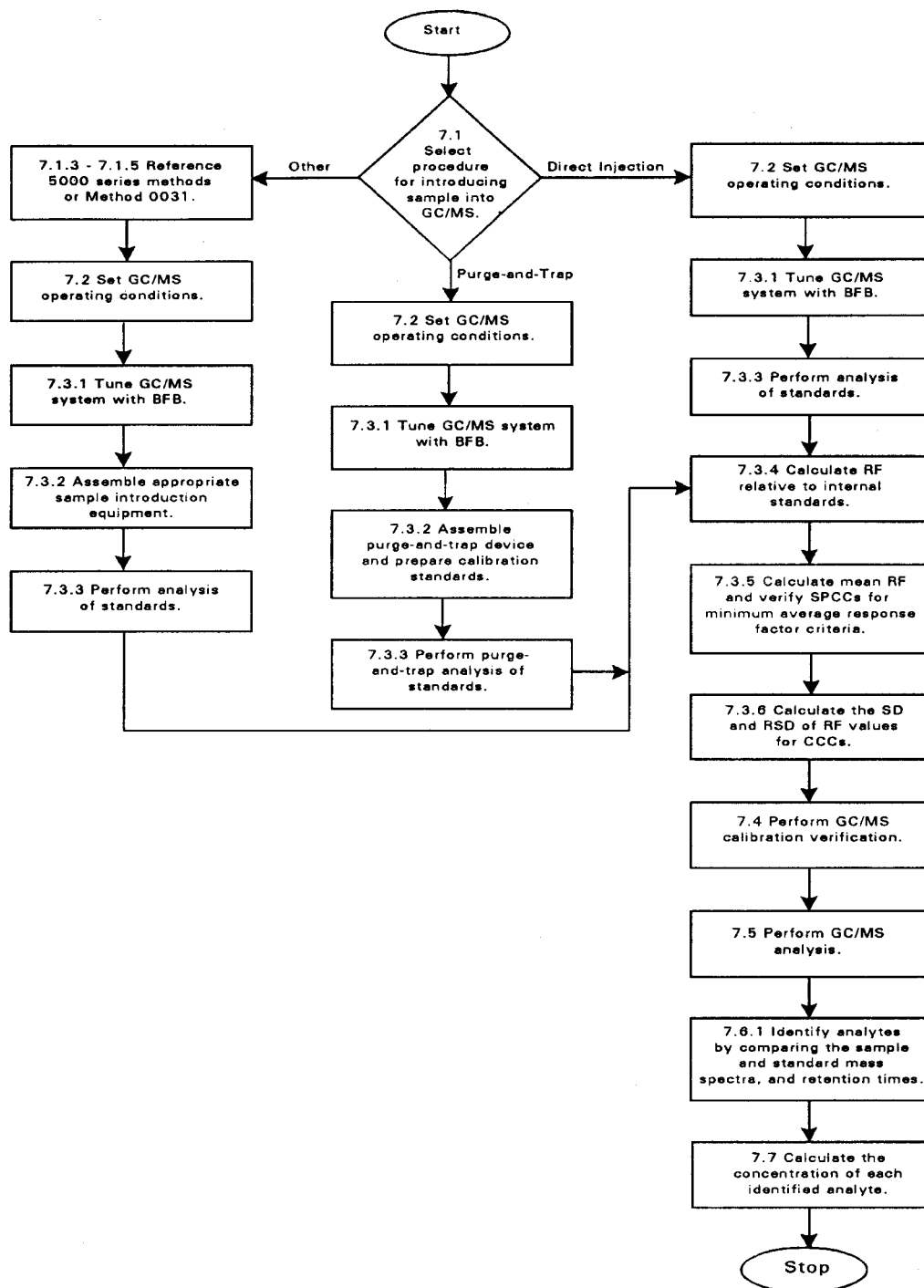


264192.

FIGURE 4  
GAS CHROMATOGRAM OF TEST MIXTURE



METHOD 8260B  
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY  
(GC/MS)



**e-MAIL RESPONSE FROM THE METHODS INFORMATION COMMUNICATION  
EXCHANGE REGARDING METHOD 8260 COMPOSITING**

Dear Mr. Spangler,

Thank you for your inquiry. We experienced problems with our voice-mail system last week, and unfortunately, we did not receive your message. We apologize for any inconvenience this may have caused you.

The use of 5 samples for compositing is mostly based on the largest syringe size appropriate for this analysis, 25-mL. For compositing you need equal volumes of each of the samples; hence, the recommendation to take a 5-mL aliquot from 5 different samples. As stated in the method, you may use a smaller number of samples, provided that equal volumes of each sample are composited, or you may use a proportionately smaller syringe.

As for using more than 5 samples, there is nothing in the method that says you can't do it. However, as volumes get smaller the associated error becomes larger. So, you will need to take precautions to minimize the errors associated with the measurement of smaller volumes. If you use a larger syringe to accommodate more than 5 samples, you need to determine what volume of aliquot to withdraw from the composite sample that will be representative of that sample.

Hope this helps.

-----  
NEWS !!! NEWS !!! NEWS !!!

OSW released Update IVB on November 27, 2000. Go to:

<http://www.epa.gov/sw-846/up4b.htm>

to find the Federal Register Notice (65 FR 70678) and download the 31 methods in this update.

The Methods Information Communication Exchange (MICE) Service

E-mail address: [mice@cpmx.saic.com](mailto:mice@cpmx.saic.com)

Phone: 703-676-4690 (leave a message) Fax: 703-903-1373

Web Site and FAQs: <http://www.epa.gov/sw-846/mice.htm>

SW-846 methods can be downloaded from the web at:

<http://www.epa.gov/sw-846/sw846.htm>

----- DISCLAIMER -----

The MICE Service is operated by Science Applications International Corporation (SAIC) under contract to the USEPA Office of Solid Waste.

All MICE Service staff are contractors. As such, they do not create or interpret USEPA policies. The role of the MICE service is to provide answers and take comments regarding the OSW methods manual known as Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846)."

## **TECHNICAL EVALUATION OF HEADSPACE GAS COMPOSITING**

# ***Technical Evaluation of Headspace Gas Compositing***

*August 2001*



# CONTENTS

FIGURES .....	iv
TABLES .....	v
ACRONYMS .....	vi
1. INTRODUCTION .....	1
2. COMPOSITING .....	2
2.1 Compositing Process .....	2
2.2 Composite Analysis and Reporting .....	3
2.2.1 Individual Analysis Example (mathematical averaging): .....	3
2.2.2 Compositing Example (physical averaging) .....	3
2.3 Compositing On Upper Confidence Limits .....	4
2.3.1 Theoretical Impact Of Compositing On The UCL <sub>90</sub> Value .....	5
2.3.2 Simulation Of Compositing .....	5
2.4 Facility Compositing Results .....	8
2.4.1 Idaho National Engineering and Environmental Laboratory UCL <sub>90</sub> Analysis .....	8
2.4.2 Idaho National Engineering and Environmental Laboratory TIC Analysis (Appendix VIII Compounds) .....	18
2.4.3 Rocky Flats Environmental Technology Site UCL <sub>90</sub> Analysis .....	18
2.4.4 Rocky Flats Environmental Technology Site TIC Analysis (Appendix VIII Compounds) .....	28
2.4.5 Conclusion .....	28
3. TENTATIVELY IDENTIFIED COMPOUNDS .....	29
3.1 Accuracy of Hazardous Waste Codes Assigned and Proper Characterization of a Waste Stream .....	29
3.2 Protection of Human Health and the Environment .....	30
4. SUMMARY .....	33

## FIGURES

Figure 1. Mean and 90% confidence interval on the mean for 5-to-1 compositing for all analytes in INEEL first/second stage sludge .....	11
Figure 2. Upper 90% confidence limits for 5-to-1 compositing for the 10 ppmv PRQL analyte group in the INEEL first/second stage sludge .....	12
Figure 3. Upper 90% confidence limits for 5-to-1 compositing for the 100 ppmv PRQL analyte group in the INEEL first/second stage sludge .....	13
Figure 4. Mean and 90% confidence interval on the mean for 10-to-1 compositing for all analytes in INEEL first/second stage sludge .....	15
Figure 5. Upper 90% confidence limits for 10-to-1 compositing for the 10 ppmv PRQL analyte group in the INEEL first/second stage sludge .....	16
Figure 6. Upper 90% confidence limits for 10-to-1 compositing for the 100 ppmv PRQL analyte group in the INEEL first/second stage sludge .....	17
Figure 7. Mean and 90% confidence interval on the mean for 5-to-1 compositing for all analytes in RFETS waste stream .....	21
Figure 8. Upper 90% confidence limits for 5-to-1 compositing for the 10 ppmv PRQL analyte group in the RFETS waste stream .....	22
Figure 9. Upper 90% confidence limits for 5-to-1 compositing for the 100 ppmv PRQL analyte group in the RFETS waste stream .....	23
Figure 10. Mean and 90% confidence interval on the mean for 20-to-1 compositing for all analytes in RFETS waste stream.....	25
Figure 11. Upper 90% confidence limits for 20-to-1 compositing for the 10 ppmv PRQL analyte group in the RFETS waste stream.....	26
Figure 12. Upper 90% confidence limits for 20-to-1 compositing for the 100 ppmv PRQL analyte group in the RFETS waste stream.....	27

## TABLES

Table 1. Upper 90% confidence limits and summary statistics .....	6
Table 2. Upper 90% confidence limits and summary statistics for all 200 containers treated together .....	6
Table 3. Concentration data sets (ppmv) used in calculation of $UCL_{90}$ values.....	7
Table 4. Analyte names and numbers for the INEEL 5-to-1 compositing 10 ppmv PRQL group .....	10
Table 5. Analyte names and numbers for the INEEL 5-to-1 compositing 100 ppmv PRQL group .....	10
Table 6. Analyte names and numbers for the INEEL 10-to-1 compositing 10 ppmv PRQL group .....	14
Table 7. Analyte names and numbers for the INEEL 10-to-1 compositing 100 ppmv PRQL group .....	14
Table 8. Analyte names and numbers for the RFETS 5-to-1 compositing 10 ppmv PRQL group.....	20
Table 9. Analyte names and numbers for the RFETS 5-to-1 compositing 100 ppmv PRQL group.....	20
Table 10. Analyte names and numbers for the RFETS 20-to-1 compositing 10 ppmv PRQL group.....	24
Table 11. Analyte names and numbers for the RFETS 20-to-1 compositing 100 ppmv PRQL group.....	24

## ACRONYMS

AK	Acceptable Knowledge
DF	Dilution Factor
DQO	Data Quality Objective
GC/MS	Gas Chromatography/Mass Spectrometry
HSG	Headspace Gas
INEEL	Idaho National Engineering and Environmental Laboratory
MDL	Method Detection Limit
MS	Mass Spectrometer
PRQL	Program Required Quantitation Limit
RFETS	Rocky Flats Environmental Technology Site
TIC	Tentatively Identified Compound
TRU	Transuranic
UCL	Upper Confidence Level
VOC	Volatile Organic Compound
WAP	Waste Analysis Plan
WIPP	Waste Isolation Pilot Plant
WWIS	WIPP Waste Information System

# Technical Evaluation of Headspace Gas Compositing

## 1. INTRODUCTION

The Waste Isolation Pilot Plan (WIPP) Hazardous Waste Facility Permit (HWFP) requires that headspace gas (HSG) samples from waste containers be taken and analyzed in accordance with the Waste Analysis Plan (WAP) requirements. HWFP Attachment B, Section B-4a(1) specifies the following data quality objective (DQO) for HSG sampling and analysis:

“To identify volatile organic compounds (VOCs) and quantify the concentrations of VOC constituents in the total waste inventory to ensure compliance with the environmental performance standards of 20 NMAC 4.1.500 (incorporating 40 CFR, §264.601(b)), and to confirm hazardous waste identification by acceptable knowledge.”

This technical evaluation of HSG compositing provides information that demonstrates how compositing meets the DQO and other requirements for HSG sampling and analysis. This evaluation includes technical justification for how compositing 1) provides WAP required and compliant data for reporting in the WIPP Waste Information System (WWIS); 2) yields 90-percent upper confidence limit (UCL<sub>90</sub>) results that are equivalent to or more conservative than individual container results for use in confirming acceptable knowledge (AK); and 3) provides data for meeting HWFP room-based VOC emissions requirements for protection of human health and the environment.

## 2. COMPOSITING

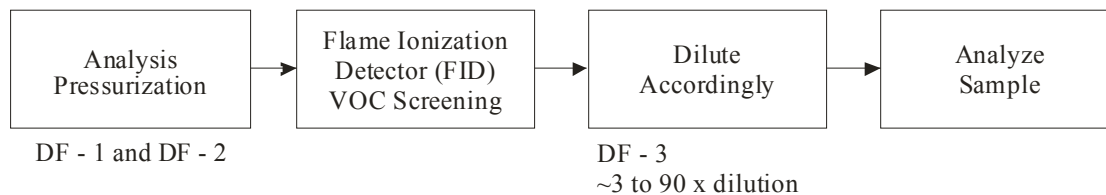
The WAP specifies that a modified Method 8260 be used for the analysis of headspace gas samples in HWFP Attachment B, Tables B-1 and B-3. SW-846 Method 8260, Section 7.5.7, provides a procedure for compositing up to 5 samples prior to analysis. Further clarification from the EPA SW-846, Methods Information Communication Exchange (MICE) Service indicates that the 5 composite procedure was “mostly based on the largest syringe size appropriate for this analysis, 25-mL.” The modifications to SW-846 Method 8260 to allow the analysis of gas samples replaces the 25 mL syringe with a 250 mL SUMMA® canister for holding the composite sample. This larger volume allows a greater number of individual containers to be represented in a single composite sample. However, the practical limitation on the transferring the individual samples to the SUMMA® canister for compositing limits the compositing to 20 individual containers (i.e., a minimum volume of 12.5 mL per sample that will be composited).

### 2.1 Compositing Process

The compositing in the laboratory process is summarized as follows. In accordance with the WAP, each container’s headspace is individually sampled into a SUMMA® canister in the field. The filled SUMMA® canister contains the individual container HSG sample at ambient pressure. The filled SUMMA® canister is then taken to the analysis laboratory.

After receipt at the laboratory, the SUMMA® canisters are pressurized on a sample manifold to approximately twice ambient pressure. This is done so a HSG aliquot can be removed from the canister without creating a vacuum (i.e., pressure less than ambient) in the canister. The dilution resulting from this pressurization is called dilution factor (DF)-1 in the diagram on this page. Equal-size aliquots are transferred from individual canisters into a separate SUMMA® canister using a gas-tight syringe. This separate SUMMA® canister is hereafter referred to as the composite SUMMA® canister.

Once all of the aliquots from the individual SUMMA® canisters have been transferred to the composite SUMMA® canister, the composite sample is ready to be delivered to the analytical instrument. The composite SUMMA® canister is then pressurized to approximately twice ambient so that aliquots can be delivered for analysis. The dilution resulting from this pressurization is called DF-2 in the diagram on this page. VOC screening is performed on each composite sample. If target analytes in the composite sample exceed the instrument calibration range, further dilution is performed (DF-3) and the diluted sample is reanalyzed. This process can be represented as follows:



The result of the analysis is the average VOC concentration in parts-per-million by volume (ppmv). Results for all target analytes and tentatively identified compounds (TICs) are reported for each individual sample that contributed to the composite. These reported results are calculated by multiplying the ppmv results of the composite sample (the average) times the product of the DFs.

$$\text{Sample result} = \text{average ppmv (composite results)} \times \text{DF-1} \times \text{DF-2} \times \text{DF-3}.$$

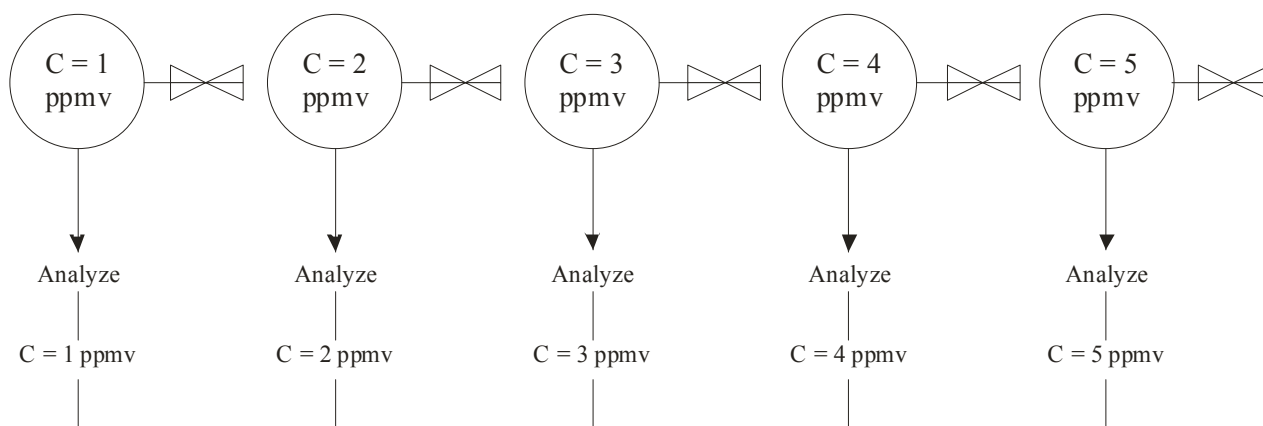
Note that DF-1 is unique for each individual sample, and DF-2 and DF-3 are the same for all samples in a composite. Thus, the reported result for each individual sample is the average concentration adjusted for a sample-specific overall dilution. It is important to note that the dilutions done to deliver the sample and to adjust sample based on the FID results are the same process that is used for individual container samples.

## 2.2 Composite Analysis and Reporting

To fully understand compositing, it is important to understand how composite sample results are determined and compare this to individual sample analyses. To accomplish this, the determination and reduction of individual results and compositing is outlined in the following two sections.

### 2.2.1 Individual Analysis Example (mathematical averaging):

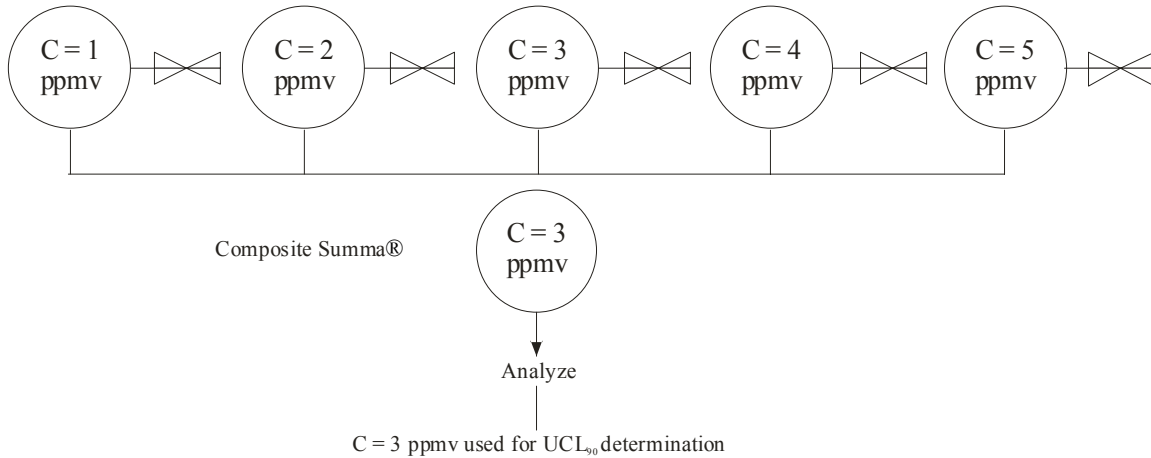
Given below is an evaluation (hypothetical) of how individual results are determined and reported for use in the determination of a UCL<sub>90</sub> value. Represented below are SUMMA® canisters with concentrations ranging from 1 to 5 ppmv. During the analysis, each SUMMA® canister is measured and the result reported. This is represented as C=1 through C=5. Before use in the UCL<sub>90</sub> value calculation, the mean is then determined. In this case, the numerical mean is 3.



Average value is used for calculating UCL<sub>90</sub>: 
$$\bar{X} = \frac{1+2+3+4+5}{5} = 3 \text{ ppmv}$$

### 2.2.2 Compositing Example (physical averaging).

An example of how the individual container samples are combined into a single composited sample and how the results for the composited sample are reported is given below. Again, the same hypothetical scenario is given. During the compositing process, identical aliquots are collected using a gas tight syringe. For five to one compositing, this can be represented as:



$$C = \frac{50 \text{ mL}(1 \text{ ppmv})}{250 \text{ mL}} + \frac{50 \text{ mL}(2 \text{ ppmv})}{250 \text{ mL}} + \frac{50 \text{ mL}(3 \text{ ppmv})}{250 \text{ mL}} + \frac{50 \text{ mL}(4 \text{ ppmv})}{250 \text{ mL}} + \frac{50 \text{ mL}(5 \text{ ppmv})}{250 \text{ mL}} = 3 \text{ ppmv}$$

where C is the concentration of the composited sample, 50 mL is the fraction collected from each SUMMA® canister and 250 mL is the SUMMA® canister volume that this fraction is introduced in.

As shown below, the resulting composite SUMMA® has a concentration of 3 ppmv, which would be the value reported in the WWIS for each of the containers that were part of the composite sample. This value is identical to the numerical average discussed earlier. The resulting value is used in the UCL<sub>90</sub> value determination.

## 2.3 Compositing On Upper Confidence Limits

This section investigates the effects of compositing HSG samples on the reported UCL<sub>90</sub> values. Specifically, does compositing result in UCL<sub>90</sub> values that are equivalent to or more conservative than UCL<sub>90</sub> values based on individual container samples.

The formula in the WAP for the UCL<sub>90</sub> value determination is given below:

$$UCL_{90} = \bar{x} + \frac{t_{0.90, n-1} s}{\sqrt{n}}, \quad (1)$$

where:

$\bar{x}$  = sample mean,

$s$  = sample standard deviation,

$t$  = value of the 90<sup>th</sup> percentile in the Student's  $t$  distribution with  $n-1$  degrees of freedom, and

$n$  = the number of samples.



### 2.3.1 Theoretical Impact Of Compositing On The UCL<sub>90</sub> Value

When individual container samples are taken and analyzed the standard deviation is calculated as:

$$s = \left[ \frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^2 \right]^{\frac{1}{2}}, \quad (2)$$

where:

$x_i$  =  $i$ th container sample measurement, and

$\bar{x}$  = container sample mean.

When samples are composited, the standard deviation is calculated using the same formula but  $x_i$  is the  $i$ th composite sample and  $\bar{x}$  is the mean of the composite samples. While the same formula is used, the standard deviation is actually the standard deviation of the composite samples, which are physical averages of  $m$  individual container samples, and so the formula can be written as:

$$s_c = \frac{s}{\sqrt{m}}, \quad (3)$$

where  $m$  is the number of individual container samples per composite.

The formula for the UCL<sub>90</sub> value then becomes:

$$UCL_{90} = \bar{x} + \frac{t_{0.90,n-1} s_c}{\sqrt{n}} = \bar{x} + \frac{t_{0.90,n-1} \frac{s}{\sqrt{m}}}{\sqrt{n}} = \bar{x} + \frac{t_{0.90,n-1} s}{\sqrt{mn}}, \quad (4)$$

where  $n$  is now the number of composite samples and  $m$  is the number of individual container samples per composite.

Suppose the number of samples is 50. Then  $m \times n = 50$  and there could be 50 “composites” of 1 individual container sample each, 10 composites of 5 individual container samples each, 5 composites of 10 individual container samples each, etc. Notice in equation (4) that the degrees of freedom ( $n-1$ ) associated with the  $t$  value is the number of composites minus 1. The values of  $m$  and  $n$  change depending on the number of composites and number of individual container samples per composite but the product  $m \times n$  does not change. Therefore, the only change in the formula is the  $t$  value. As the degrees of freedom decrease (or as  $n$  decreases) the  $t$  value increases. The theoretical result is that for a fixed sample size and constant standard deviation, compositing causes an increase in the UCL<sub>90</sub> value. This increase is due to the change in the Student's  $t$  value.

It is important to note that equation (1), which is reproduced from the WAP, is identical to equation (4). However, it needs to be clear that  $n$  is the number of composite samples, not the total number of samples, and the standard deviation is calculated using the composite sample measurements.

### 2.3.2 Simulation Of Compositing

In practice, the standard deviation is not constant and therefore cases may occur where the UCL<sub>90</sub> value slightly decreases with compositing (i.e., versus individual container sampling) simply due to the random error in the estimation of the standard deviation. However, even in this case, the UCL<sub>90</sub> value for compositing will be equivalent to one based on individual container samples and will be an appropriate estimate of the UCL<sub>90</sub> value.

A data set of 200 sample concentrations of 1,1,1-Trichloroethane from 200 containers of graphite waste previously sampled and analyzed as individual container samples was obtained to use as an example of how the  $UCL_{90}$  value can vary with compositing. This data set was split into four data sets of 50 measurements each. Compositing was simulated by calculating averages based on five and ten individual container samples per composite sample. The summary statistics and  $UCL_{90}$  values for each of the four data sets (i.e., the individual container, 5-composite, and 10-composite samples) are given in Table 1. The raw data that were used to perform these calculations are presented in Table 3.

As shown in Table 1, the  $UCL_{90}$  value increases with compositing for the first, second, and fourth data sets, but decreases slightly for the third data set. However, the composite results for the third data set remain equivalent and the  $UCL_{90}$  value only decreases slightly because of the variability in the standard deviation (the standard deviation for the composited data sets is much smaller than any of the other standard deviations due to random error). Table 2 presents the results of compositing when all 200 measurements are treated as a single population and when 10 container composites and 20 container composites are simulated. In this case, the  $UCL_{90}$  value increases with compositing.

In four of the five analyses summarized in Tables 1 and 2, the  $UCL_{90}$  value increases with compositing. The exception is a very slight decrease.

Table 1. Upper 90% confidence limits and summary statistics

Statistic	1 <sup>st</sup> 50 drums	5 drum comp	10 drum comp	2 <sup>nd</sup> 50 drums	5 drum comp	10 drum comp	3 <sup>rd</sup> 50 drums	5 drum comp	10 drum comp	4 <sup>th</sup> 50 drums	5 drum comp	10 drum comp
Mean (ppmv)	15.95	15.95	15.95	29.45	29.45	29.45	24.18	24.18	24.18	32.26	32.26	32.26
Std. Dev.	28.09	16.25	14.34	26.45	16.69	13.10	24.39	6.54	4.30	42.59	28.28	27.57
N	50	10	5	50	10	5	50	10	5	50	10	5
T	1.300	1.383	1.533	1.300	1.383	1.533	1.300	1.383	1.533	1.300	1.383	1.533
<b><math>UCL_{90}</math> (ppmv)</b>	<b>21.11<sup>a</sup></b>	<b>23.06</b>	<b>25.78</b>	<b>34.32<sup>a</sup></b>	<b>36.76</b>	<b>38.44</b>	<b>28.67<sup>a</sup></b>	<b>27.04</b>	<b>27.13</b>	<b>40.08<sup>a</sup></b>	<b>44.62</b>	<b>51.16</b>

a.  $UCL_{90}$  value is based on individual container measurements, i.e., no compositing,  $m = 1$ .

b. Comp = Composite

Table 2. Upper 90% confidence limits and summary statistics for all 200 containers treated together

Statistic	All 200 containers	10 drum composite	20 drum composite
Mean (ppmv)	25.46	25.46	25.46
Standard deviation	31.60	16.85	15.59
N	200	20	10
T	1.282	1.328	1.383
<b><math>UCL_{90}</math> (ppmv)</b>	<b>28.32<sup>a</sup></b>	<b>30.46</b>	<b>32.28</b>

a.  $UCL_{90}$  value is based on individual container measurements, i.e., no compositing,  $m = 1$ .

Table 3. Concentration data sets (ppmv) used in calculation of UCL<sub>90</sub> values

1 <sup>st</sup> 50 drums	5 drum comp means	10 drum comp means	2 <sup>nd</sup> 50 drums	5 drum comp means	10 drum comp means	3 <sup>rd</sup> 50 drums	5 drum comp means	10 drum comp means	4 <sup>th</sup> 50 drums	5 drum comp means	10 drum comp means
0.500			18.000			38.000			4.500		
0.081			8.800			11.000			75.000		
0.035			48.000			28.000			14.000		
0.032			12.000			12.000			39.000		
0.056	0.141		7.200	18.800		37.000	25.200		11.000	28.700	
0.032			33.000			36.000			7.500		
0.058			74.000			31.000			110.000		
0.043			79.000			38.000			40.000		
0.570			35.000			23.000			180.000		
0.039	0.148	0.145	30.000	50.200	34.500	17.000	29.000	27.100	39.000	75.300	52.000
0.038			29.000			11.000			63.000		
0.058			11.000			21.000			7.000		
0.032			12.000			40.000			140.000		
0.310			5.100			14.000			20.000		
0.087	0.105		24.000	16.220		14.000	20.000		52.000	56.400	
0.071			17.000			13.000			68.000		
0.032			2.200			16.000			38.000		
0.032			23.000			6.100			38.000		
53.000			16.000			140.000			120.000		
22.000	15.027	7.566	59.000	23.440	19.830	8.500	36.720	28.360	6.700	54.140	55.270
20.000			8.700			7.700			23.000		
8.500			110.000			22.000			27.000		
8.200			8.200			73.000			3.100		
13.000			8.100			3.700			100.000		
0.210	9.982		18.000	30.600		54.000	32.080		89.000	48.420	
9.000			11.000			22.000			43.000		
110.000			6.900			32.000			38.000		
10.000			10.000			27.000			100.000		
17.000			27.000			13.000			63.000		
0.410	29.282	19.632	3.200	11.620	21.110	9.100	20.620	26.350	11.000	51.000	49.710
8.200			93.000			10.000			6.500		
31.000			87.000			1.600			0.071		
0.068			2.300			24.000			0.079		
0.035			74.000			31.000			0.077		
98.000	27.461		63.000	63.860		45.000	22.320		0.073	1.360	
0.210			29.000			12.000			0.085		
1.500			14.000			4.100			0.052		
0.042			32.000			9.700			0.057		
0.280			66.000			51.000			0.042		
4.500	1.306	14.384	43.000	36.800	50.330	2.300	15.820	19.070	0.220	0.091	0.726
0.083			42.000			0.960			0.048		
0.032			29.000			37.000			0.063		
0.044			33.000			34.000			0.039		
97.000			13.000			19.000			0.430		
59.000	31.232		20.000	27.400		3.600	18.912		0.750	0.266	
62.000			11.000			7.500			0.032		
47.000			11.000			5.100			0.052		
45.000			32.000			80.000			7.300		
16.000			3.000			2.100			11.000		
54.000	44.800	38.016	21.000	15.600	21.500	11.000	21.140	20.026	16.000	6.877	3.571

## 2.4 Facility Compositing Results

A comparison of means and  $UCL_{90}$  values for both composite and individual container samples for data sets collected at the Idaho National Engineering and Environmental Laboratory (INEEL) and the Rocky Flats Environmental Technology Site (RFETS) was conducted as part of this technical evaluation. The data sets used represent the largest mixed waste stream (i.e., the INEEL first/second stage sludge) and the largest non-mixed waste stream (i.e., the RFETS combustible/plastic debris) where both composited and individual container results are available. In addition to the mean and  $UCL_{90}$  value evaluations, a discussion of TICs for these waste streams is provided. It is important to note that TICs have been detected in both composite and individual analysis samples for each of these waste streams; however, not all of the detected TICs are found in Appendix VIII. To date the frequency for Appendix VIII compounds has been far below the 25% threshold level and no target analytes have been added. In addition, no hazardous waste numbers have been added as a result of TIC identification.

### 2.4.1 Idaho National Engineering and Environmental Laboratory $UCL_{90}$ Analysis

In a further attempt to illustrate the effect of compositing, comparisons were made between composited results and individual container results for the first/second stage sludge waste. This is possible because, for this waste stream, analytical results from composited samples and individual container samples exist.

The individual container sample data are all of the validated measurements from the first/second stage sludge waste stream, which are from 90 individually analyzed samples. The composite data are based on validated composited results from the first/second stage sludge waste stream. The data for this waste stream were evaluated to compare the effects of 5-to-1 compositing and 10-to-1 compositing to individual container samples. For the 5-to-1 compositing evaluation, all of the individual container results (i.e., 90) were used. To provide a statistically comparable composited data set, 10 separate sets of eighteen 5-container composite results were randomly selected from the sixty-nine 5-drum composite samples for the waste stream. The average sample mean and standard deviation calculated from the 10 separate sets were used as the best estimate of the mean and standard deviation for a typical set of eighteen 5-drum composite results. These average values for the mean and standard deviation were used in the additional calculations (i.e., to calculate the  $UCL_{90}$  values and 90% confidence interval on the mean).

There are only seven 10-container composites representing 70 containers available for the 10-to-1 compositing evaluation. To provide a comparable group of containers for the 10-to-1 compositing evaluation, an additional three 9-container composites were randomly selected from the sixteen 9-container composites for this waste stream. These together (i.e., the seven 10-container and three 9-container composites) represent 97 containers, which provide a statistically comparable sample to the 90 individual container samples.

There are 28 target analytes for the INEEL first/second stage sludge waste stream. These analytes are denoted by an analyte number (i.e., 1 through 28) in the figures that follow because the analyte names are too long to be included on the figures. The  $UCL_{90}$  value results for the data sets were separated into 2 analyte groups based on the Program Required Quantitation Limit (PRQL): 1) analytes with a PRQL of 10 ppmv and 2) analytes with a PRQL of 100 ppmv. The PRQL is the level where the HWFP requires AK information to be reevaluated based on the results of headspace gas sampling and analysis. It is also important to note that any concentrations that are below the PRQL are only estimated concentrations. This is particularly important for the evaluations presented here because most of the concentration data is below the PRQL. Tables 4 and 5 provide the analyte names and numbers for Figures 1 through 3, which are for the 5 to 1 compositing data set. Tables 6 and 7 provide the analyte names and numbers for

Figures 4 through 6, which are for the 10 to 1 compositing data set. The analytes for all of the analyte groups are ordered based on increasing  $UCL_{90}$  values for the composite results.

Figure 1 presents the mean concentration and 90% confidence interval on the mean for 5-to-1 compositing and individual container sample results for all analytes. For every analyte except methanol (analyte 28), the confidence intervals on the mean overlap leading to the conclusion that there are no statistically significant differences at the 90% confidence level between 5-to-1 compositing and individual container samples. For methanol, the compositing confidence interval on the mean is higher than the individual container sample confidence interval on the mean. In this case, the methanol result from compositing is more conservative than the individual container sample result. This is because methanol was only detected in one sample from the population (less than 1%), which was a composited sample. Both of the means (i.e., composited and individual container), including the confidence interval on the mean, are an order of magnitude less than the PRQL.

Figures 2 and 3 show the calculated  $UCL_{90}$  values for the 10 ppmv and 100 ppmv PRQL analyte groups for five-container compositing, respectively. In all cases, there are small differences between  $UCL_{90}$  values for the composites and  $UCL_{90}$  values for the individual containers, or the  $UCL_{90}$  values for composites are larger than those for the individual containers. These figures, along with the mean and confidence interval on the mean figure, demonstrate that 5-to-1 compositing results in values that are equivalent to or more conservative than those for individual container results.

Figures 4 through 6 present similar results for 10-to-1 compositing. Again, the confidence intervals on the mean overlap for all but methanol indicating that there are no statistically significant differences at the 90% confidence level on the mean. For methanol (analyte 28) in the 10-container compositing results, the composited mean with the confidence interval on the mean is again higher than the individual container mean with the confidence interval on the mean. Once more, both of the methanol results are an order of magnitude less than PRQL. The  $UCL_{90}$  value figures for the 10-to-1 compositing continue demonstrate the conclusion that compositing results in measurements that are equivalent to or greater than those for individual container samples.

Table 4. Analyte names and numbers for the INEEL 5-to-1 compositing 10 ppmv PRQL group

Analyte Name	Analyte Number
Cyclohexane	1
1,1,2,2-Tetrachloroethane	2
1,2-Dichloroethane	3
Bromoform	4
Chlorobenzene	5
1,3,5-Trimethylbenzene	6
Ethyl ether	7
1,2,4-Trimethylbenzene	8
cis-1,2-Dichloroethylene	9
o-Xylene	10
Ethylbenzene	11
Methylene chloride	12
Benzene	13
1,1-Dichloroethylene	14
m&p-Xylene	15
Chloroform	16
1,1,2-Trichloro-1,2,2-trifluoroethane	17
1,1-Dichloroethane	18
Toluene	19
Tetrachloroethylene	20
Carbon tetrachloride	21
Trichloroethylene	22
1,1,1-Trichloroethane	23

Table 5. Analyte names and numbers for the INEEL 5-to-1 compositing 100 ppmv PRQL group

Analyte Name	Analyte Number
Methyl isobutyl ketone	24
Methyl ethyl ketone	25
Butanol	26
Acetone	27
Methanol	28

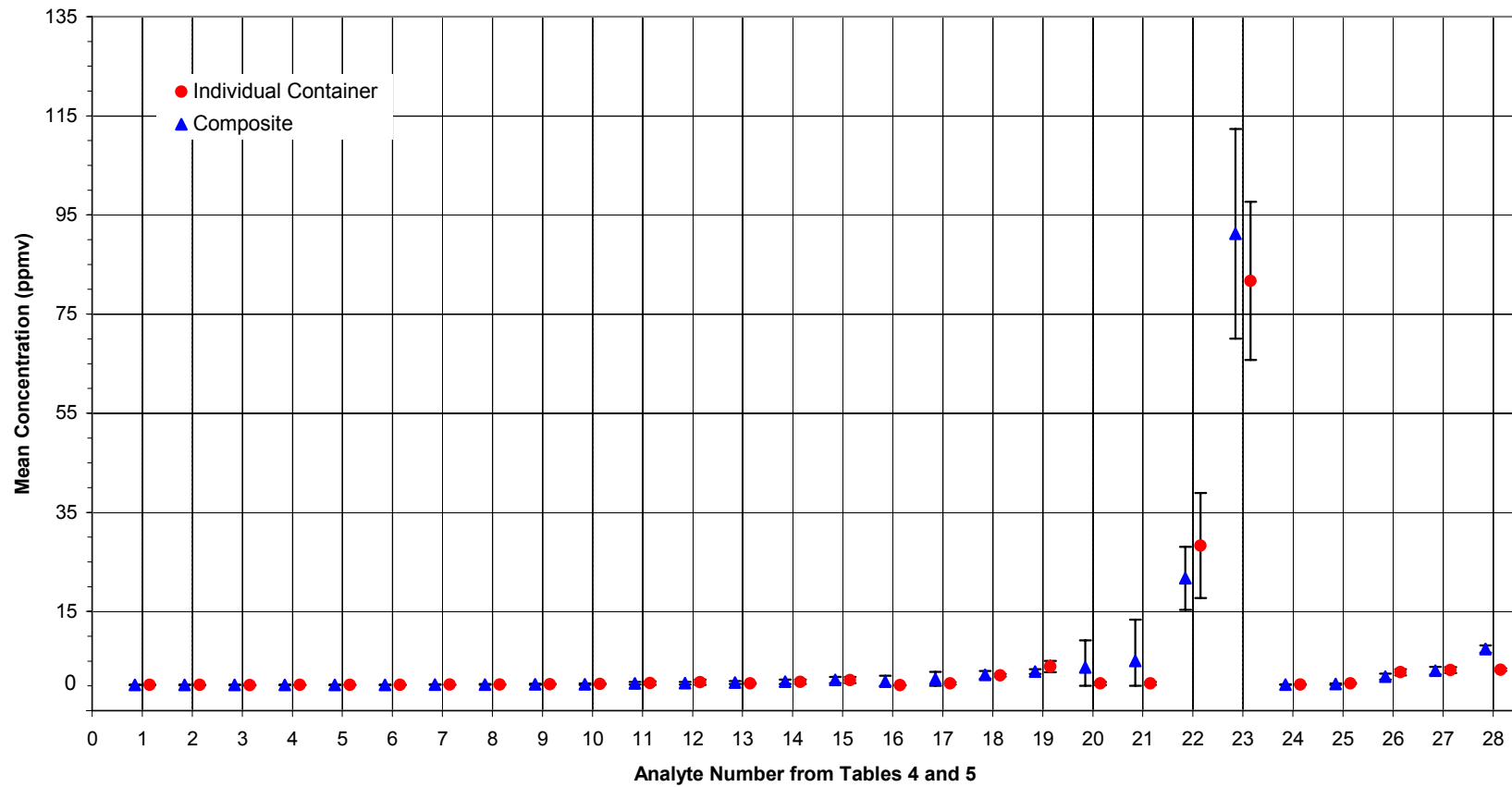


Figure 1. Mean and 90% confidence interval on the mean for 5-to-1 compositing for all analytes in INEEL first/second stage sludge

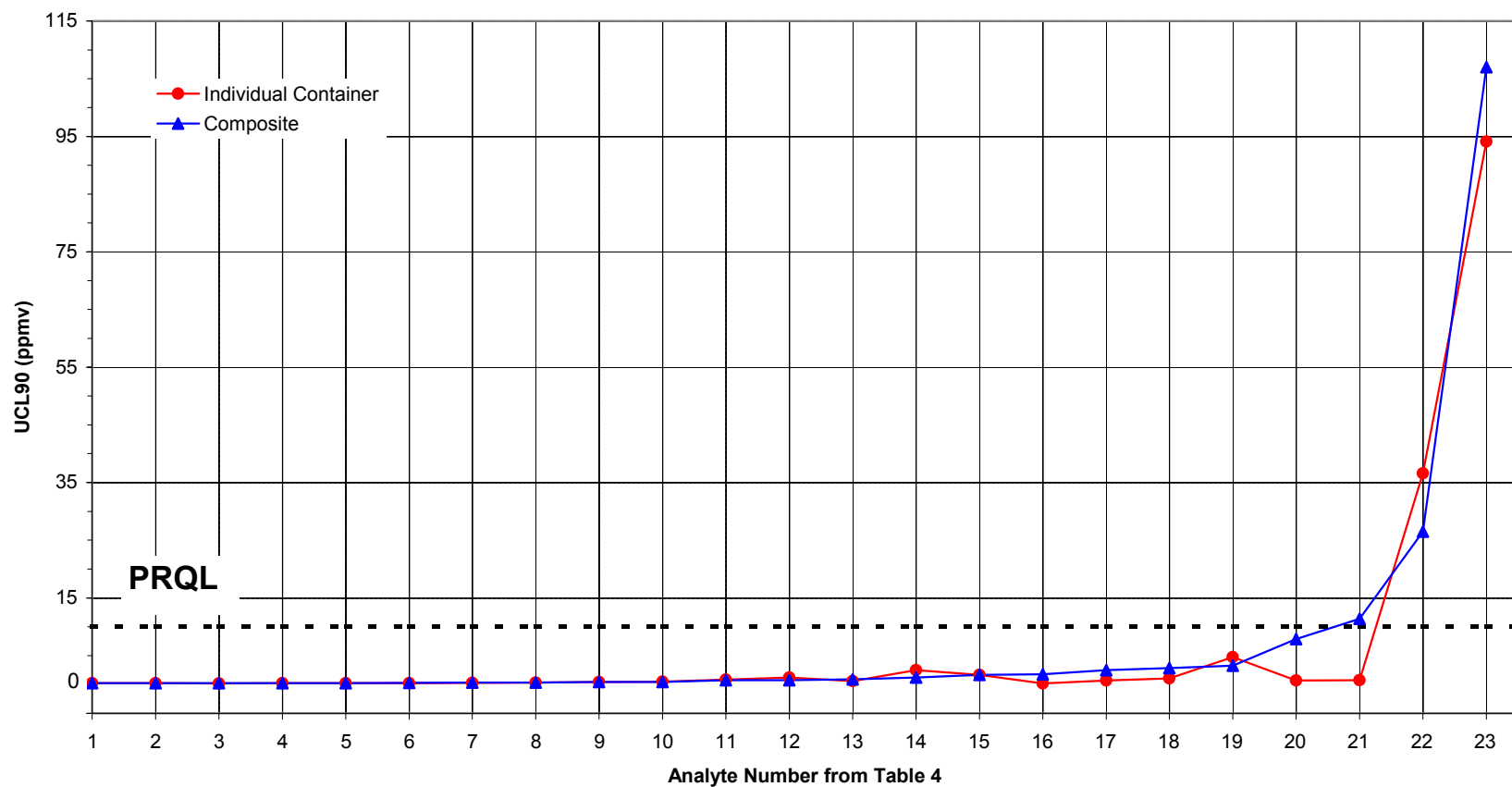


Figure 2. Upper 90% confidence limits for 5-to-1 compositing for the 10 ppmv PRQL analyte group in the INEEL first/second stage sludge



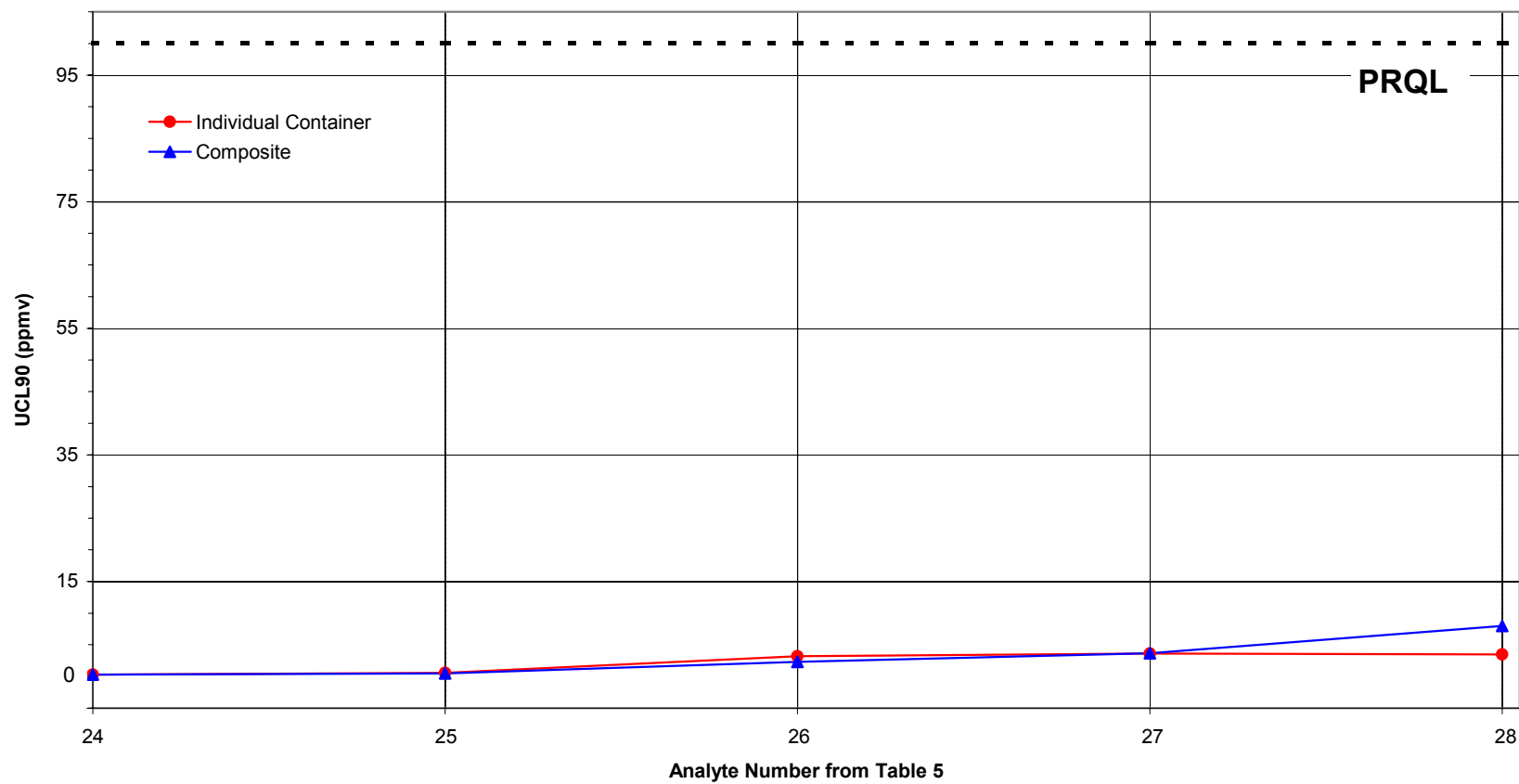


Figure 3. Upper 90% confidence limits for 5-to-1 compositing for the 100 ppmv PRQL analyte group in the INEEL first/second stage sludge

Table 6. Analyte names and numbers for the INEEL 10-to-1 compositing 10 ppmv PRQL group

Analyte Name	Analyte Number
Chloroform	1
1,2-Dichloroethane	2
1,3,5-Trimethylbenzene	3
1,1,2,2-Tetrachloroethane	4
1,2,4-Trimethylbenzene	5
Carbon tetrachloride	6
Bromoform	7
Chlorobenzene	8
cis-1,2-Dichloroethylene	9
Cyclohexane	10
Ethyl ether	11
o-Xylene	12
Methylene chloride	13
Benzene	14
Tetrachloroethylene	15
Ethylbenzene	16
1,1-Dichloroethane	17
m&p-Xylene	18
1,1-Dichloroethylene	19
Toluene	20
1,1,2-Trichloro-1,2,2-trifluoroethane	21
Trichloroethylene	22
1,1,1-Trichloroethane	23

Table 7. Analyte names and numbers for the INEEL 10-to-1 compositing 100 ppmv PRQL group

Analyte Name	Analyte Number
Methyl isobutyl ketone	24
Methyl ethyl ketone	25
Butanol	26
Acetone	27
Methanol	28

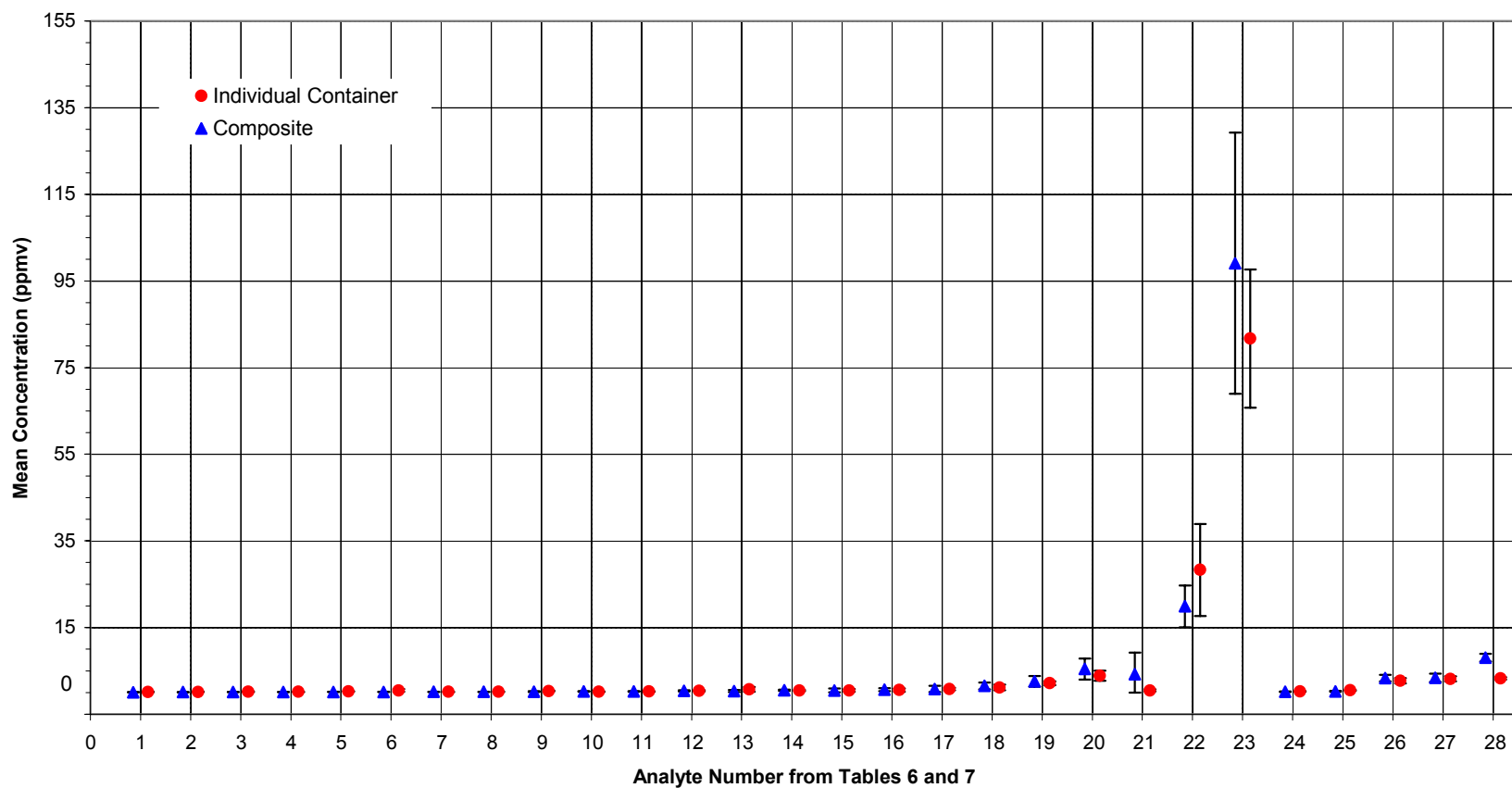


Figure 4. Mean and 90% confidence interval on the mean for 10-to-1 compositing for all analytes in INEEL first/second stage sludge

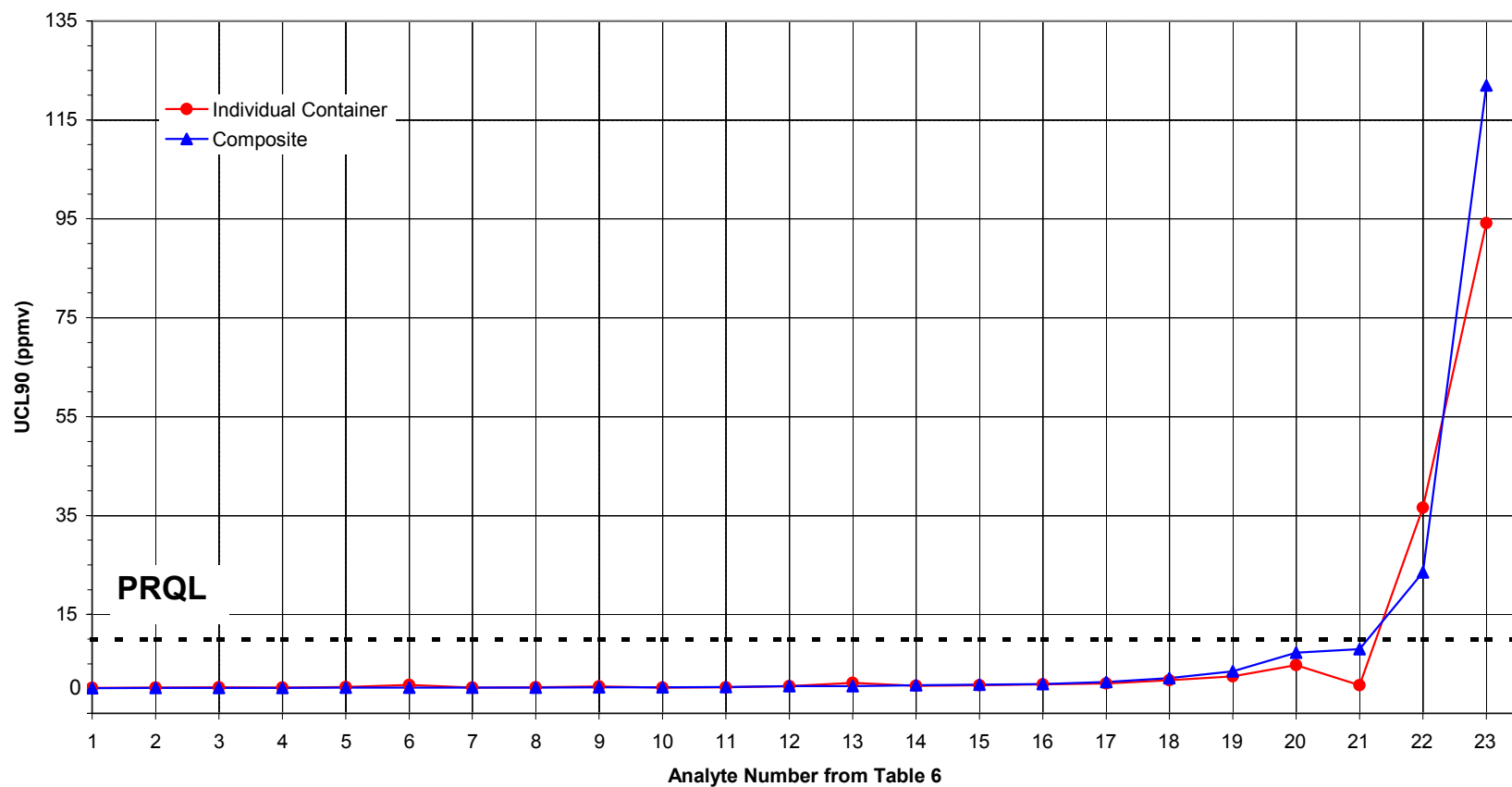


Figure 5. Upper 90% confidence limits for 10-to-1 compositing for the 10 ppmv PRQL analyte group in the INEEL first/second stage sludge

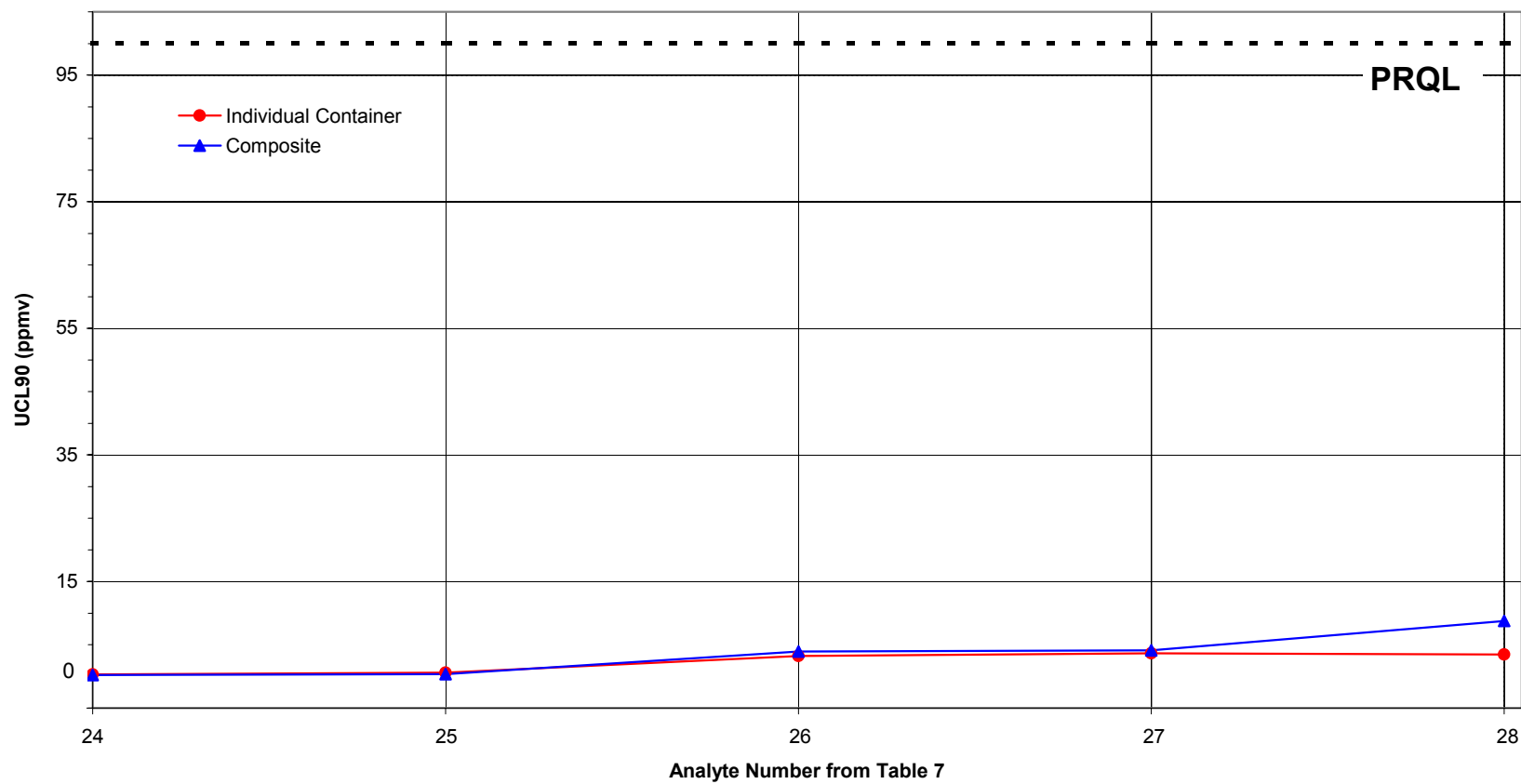


Figure 6. Upper 90% confidence limits for 10-to-1 compositing for the 100 ppmv PRQL analyte group in the INEEL first/second stage sludge

#### **2.4.2 Idaho National Engineering and Environmental Laboratory TIC Analysis (Appendix VIII Compounds)**

For first/second stage sludge, no Appendix VIII TICs were identified in either the composite data set or the individual container data set.

#### **2.4.3 Rocky Flats Environmental Technology Site UCL<sub>90</sub> Analysis**

The individual container data set for this evaluation consists of 1137 individual container sample results from the RFETS non-mixed combustible/plastic debris waste stream. The composited data set for this evaluation consists of 183 composite sample results, representing 1042 containers for the same waste stream. The composite samples consist of composites of as few as 2 containers and as many as 19 containers with about 65% (119) being 5-container composites representing 595 containers from the waste stream. These 595 containers represent 57% of the 1042 containers analyzed using composite samples. The next largest aggregate of containers is the 17-to-1 through 19-to-1 container composites representing a total of 239 (23%) of the 1042 containers analyzed using composite samples.

The data for this waste stream were evaluated to compare the effects of 5-to-1 compositing and 20-to-1 compositing to individual container samples. For the 5-to-1 compositing evaluation, all of the 5-container composites (i.e., 119) were used. To provide a statistically comparable individual container data set, 10 separate sets of 595 individual container results were randomly selected from the 1137 individual container samples for the waste stream. The average sample mean and standard deviation calculated from the 10 separate sets were used as the best estimate of the mean and standard deviation for a typical set of 595 containers. These average values for the mean and standard deviation were used in the additional calculations (i.e., to calculate the UCL<sub>90</sub> values and 90% confidence interval on the mean).

For the RFETS non-mixed combustible/plastic debris waste stream, there are 29 target analytes. The analyte that is not on the WAP required target analyte list is carbon disulfide (added to RFETS target analyte list prior to issuance of the WAP). These analytes are denoted by an analyte number (i.e., 1 through 29) in the figures that follow because the analyte names are too long to be included on the figures. As was the case for the INEEL data, the UCL<sub>90</sub> value results for the RFETS data sets were separated into 2 analyte groups based on the PRQL: 1) analytes with a PRQL of 10 ppmv and 2) analytes with a PRQL of 100 ppmv. Once more, it is important to note that any concentrations that are below the PRQL are only estimated concentrations. This is even more important for the RFETS evaluations because the waste stream is a non-mixed waste stream where, on average, more than 95% of the detections are below the PRQL. Tables 8 and 9 provide the analyte names and numbers for Figures 7 through 9, which are for the 5-to-1 compositing data set. Tables 10 and 11 provide the analyte names and numbers for Figures 10 through 12, which are for the 20-to-1 compositing data set. The analytes for all of the analyte groups are ordered based on increasing UCL<sub>90</sub> values for the composite results and because of this, the order of the RFETS analytes is different than the order used for the INEEL analytes.

Figure 7 presents the mean concentration and 90% confidence interval on the mean for 5-to-1 compositing and individual container samples for all analytes. The confidence interval on the mean overlaps for all but 4 analytes, leading to the conclusion that there are no statistically significant differences in average analyte concentration between composites and individual container samples for these cases, although the spread of data values may vary. In the four cases where the confidence interval on the mean overlap does not occur, two analytes, carbon disulfide (analyte 23) and ethyl ether (analyte 20), exhibit significantly higher values for the composite sample confidence interval on the mean, suggesting that the composite sample results tend to be more conservative in estimating mean concentration. The two cases where the composited sample confidence interval on the mean lies below that of the non-composite sample occur for two analytes with detection rates of less than 1%, which is an extremely low detection rate. Ethyl ether also shows a detection rate of less than 1%. Variability in the

reported method detection limits contributed more to the observed differences than the single detected concentration values because, following the WAP requirements, one half of the detection limit is used for the mean calculation when an analyte is not detected.

Figures 8 and 9 show the calculated  $UCL_{90}$  values for the 10 ppmv and 100 ppmv PRQL analyte groups for 5-container compositing, respectively. With the exception of cyclohexane (analyte 11), the composite sample  $UCL_{90}$  values were consistently equivalent to or greater than the individual container  $UCL_{90}$  values. The uncharacteristically larger individual container  $UCL_{90}$  for cyclohexane is because the composite samples and the individual container results are from different physical sets of containers. Because there were so few cyclohexane detections in both the composited and individual container data sets, a single large value among the remaining very small values (i.e., one half of the detection limit) in the individual container data set skews the final results. However, this phenomenon is not significant because it only occurs in cases where there are primarily non-detectable concentrations resulting in  $UCL_{90}$  values that are well below the PRQL, as in this case. Had both of the sets of physical containers that were sampled contained similar concentration ranges in the headspace, the composite and individual container  $UCL_{90}$  values would have been equivalent. In all cases other than cyclohexane, there are small differences between  $UCL_{90}$  values for the composites and  $UCL_{90}$  values for the individual containers, or the  $UCL_{90}$  values for composites are larger than those for the individual containers. These figures, along with the mean and confidence interval on the mean figure, demonstrate that 5-to-1 compositing results in values that are equivalent to or more conservative than those for individual container results.

RFETS has not conducted any full 20-to-1 composite samples; therefore the results from the 17-, 18-, and 19-to-1 composite samples (13 samples) will be used to evaluate the 20-to-1 compositing case. The composites in this evaluation represented a total of 239 (23%) of the 1042 source drums

Similar to the 5-to-1 evaluation, 10 separate sets of 239 individual container results were randomly selected from the 1137 individual container samples for the waste stream to provide a statistically comparable individual container data set. The average sample mean and standard deviation calculated from the 10 separate sets were used as the best estimate of the mean and standard deviation for a typical set of 239 containers. These average values for the mean and standard deviation were used in the additional calculations (i.e., to calculate the  $UCL_{90}$  values and 90% confidence interval on the mean).

Figures 10 through 12 present similar results for 20-to-1 compositing as those presented for the 5-to-1 compositing evaluation. In the mean with the confidence interval on the mean graph, Figure 10, all but two of the analyte confidence intervals on the mean overlap, once again leading to the conclusion that there are no statistically significant differences in average analyte concentration between composites and non-composites for these cases, although the spread of data values may vary. In both cases where the confidence interval on the mean overlap does not occur, the analytes, carbon disulfide (analyte 22) and acetone (analyte 28), exhibit higher values for the composite sample confidence interval on the mean, suggesting that the composite sample results tend to be more conservative in estimating mean concentration.

Figures 11 and 12 show the  $UCL_{90}$  results for the 20-to-1 compositing evaluation. The 20-to-1 compositing  $UCL_{90}$  results for cyclohexane (analyte 16) show the same phenomenon described for the 5-to-1 results and the  $UCL_{90}$  values for the remaining analytes continue to demonstrate the conclusion that compositing results in measurements that are equivalent to or greater than those for non-compositing.

Table 8. Analyte names and numbers for the RFETS 5-to-1 compositing 10 ppmv PRQL group

Analyte Name	Analyte Number
Tetrachloroethylene	1
cis-1,2-Dichloroethylene	2
1,3,5-Trimethylbenzene	3
Trichloroethylene	4
1,1-Dichloroethane	5
1,2,4-Trimethylbenzene	6
Carbon tetrachloride	7
1,1,1-Trichloroethane	8
1,2-Dichloroethane	9
o-Xylene	10
Cyclohexane	11
1,1,2-Trichloro-1,2,2-trifluoroethane	12
Bromoform	13
Chlorobenzene	14
1,1-Dichloroethylene	15
1,1,2,2-Tetrachloroethane	16
Ethylbenzene	17
Methylene chloride	18
Chloroform	19
Ethyl ether	20
Benzene	21
m&p-Xylenes	22
Carbon disulfide	23
Toluene	24

Table 9. Analyte names and numbers for the RFETS 5-to-1 compositing 100 ppmv PRQL group

Analyte Name	Analyte Number
Methyl isobutyl ketone	25
Methyl ethyl ketone	26
Butanol	27
Acetone	28
Methanol	29



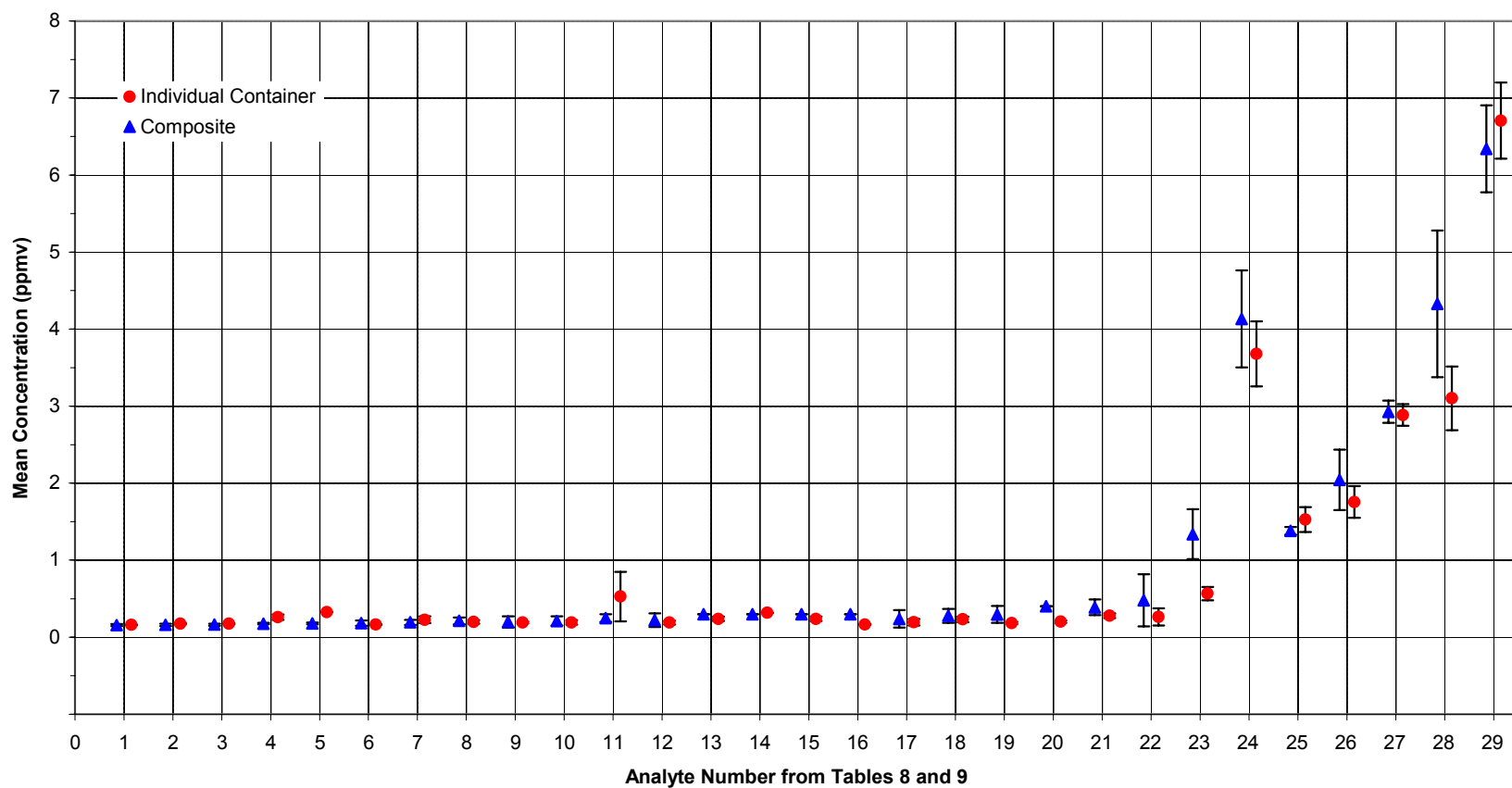


Figure 7. Mean and 90% confidence interval on the mean for 5-to-1 compositing for all analytes in RFETS waste stream

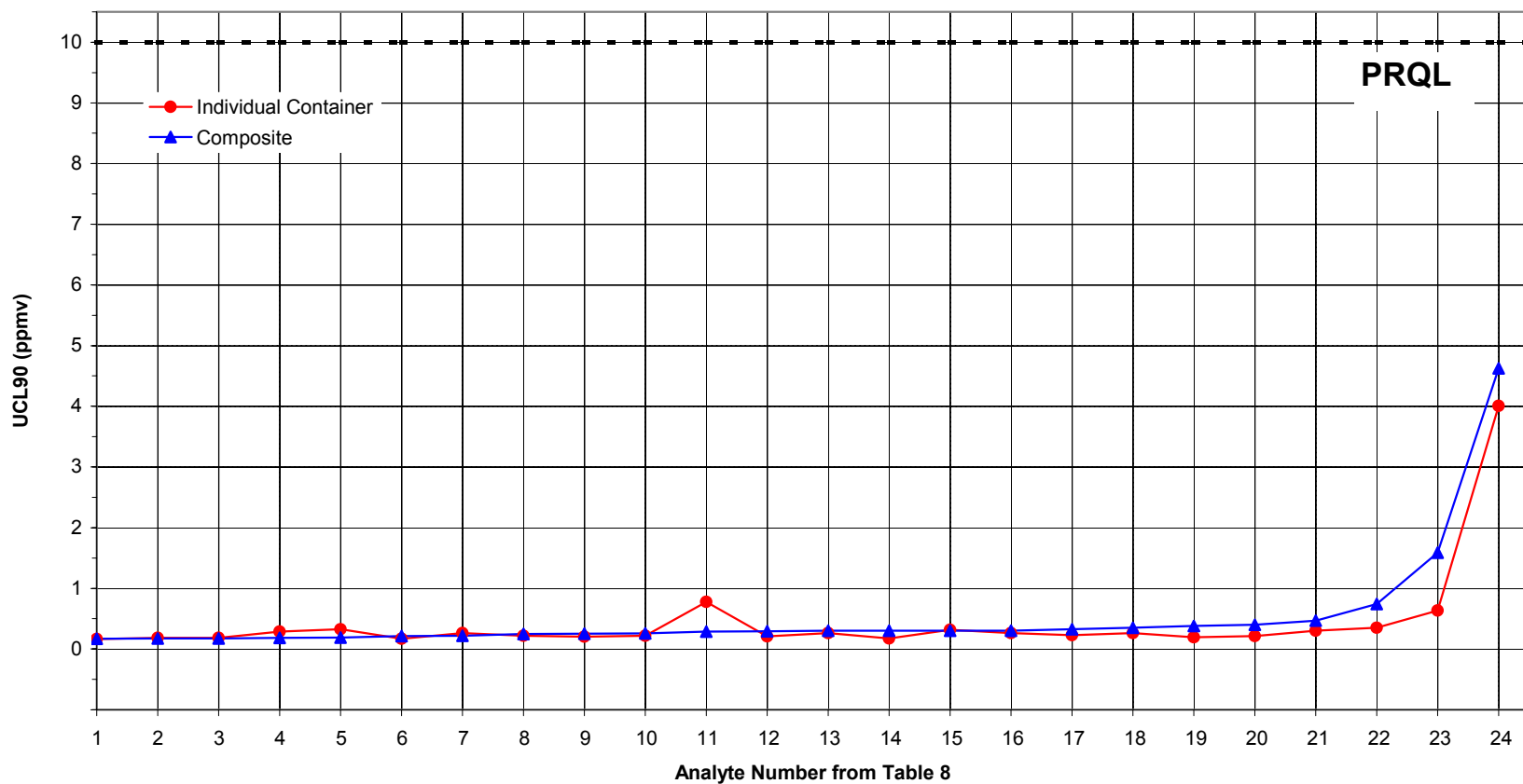


Figure 8. Upper 90% confidence limits for 5-to-1 compositing for the 10 ppmv PRQL analyte group in the RFETS waste stream

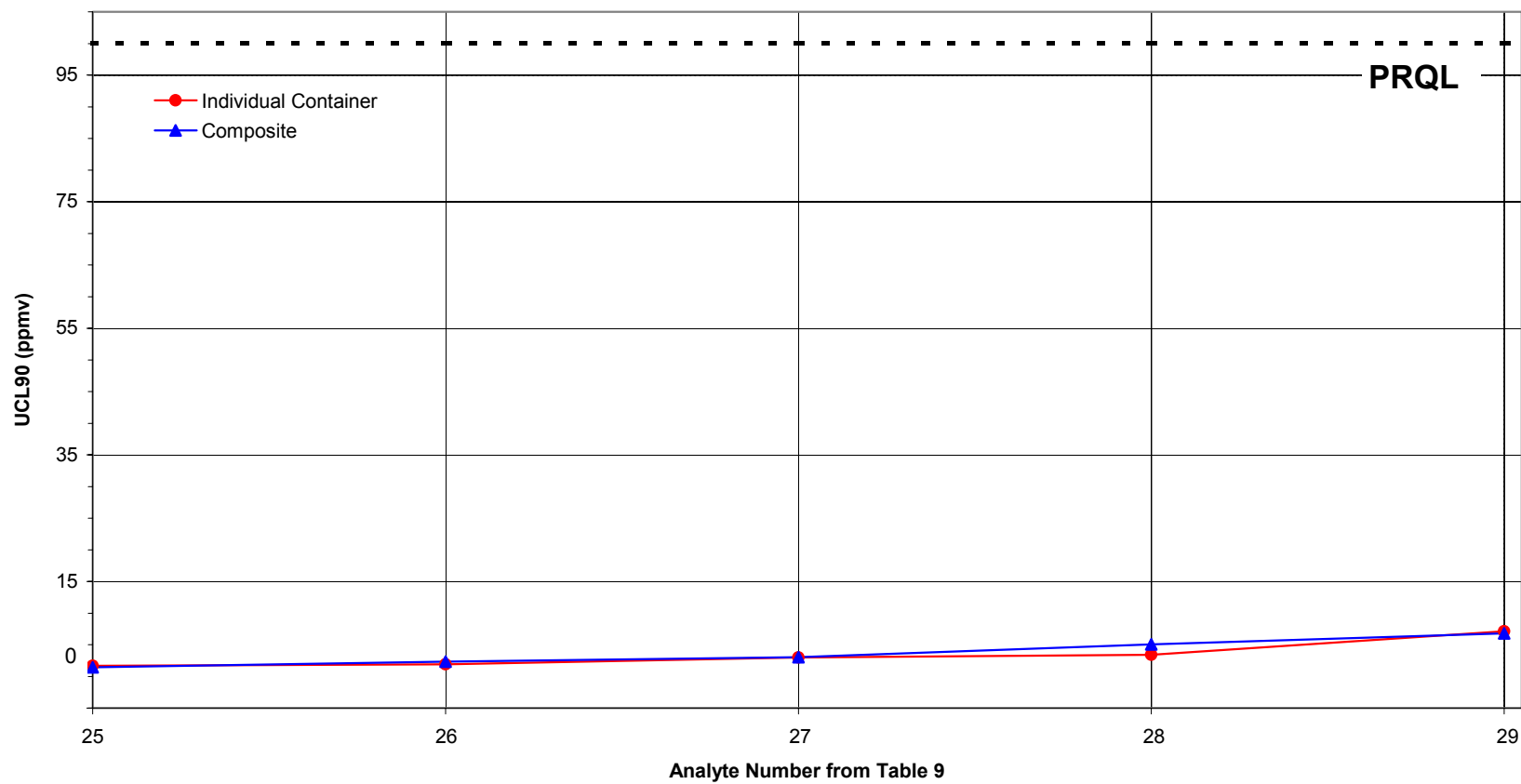


Figure 9. Upper 90% confidence limits for 5-to-1 compositing for the 100 ppmv PRQL analyte group in the RFETS waste stream

Table 10. Analyte names and numbers for the RFETS 20-to-1 compositing 10 ppmv PRQL group

Analyte Name	Analyte Number
Bromoform	1
Chlorobenzene	2
cis-1,2-Dichloroethylene	3
1,1,2,2-Tetrachloroethane	4
Tetrachloroethylene	5
1,1-Dichloroethylene	6
1,3,5-Trimethylbenzene	7
1,2,4-Trimethylbenzene	8
1,2-Dichloroethane	9
1,1,2-Trichloro-1,2,2-trifluoroethane	10
Trichloroethylene	11
1,1-Dichloroethane	12
Carbon tetrachloride	13
Ethyl ether	14
o-Xylene	15
Cyclohexane	16
Ethylbenzene	17
Methylene chloride	18
Benzene	19
1,1,1-Trichloroethane	20
Chloroform	21
Carbon disulfide	22
m&p-Xylene	23
Toluene	24

Table 11. Analyte names and numbers for the RFETS 20-to-1 compositing 100 ppmv PRQL group

Analyte Name	Analyte Number
Methyl isobutyl ketone	25
Methyl ethyl ketone	26
Butanol	27
Acetone	28
Methanol	29

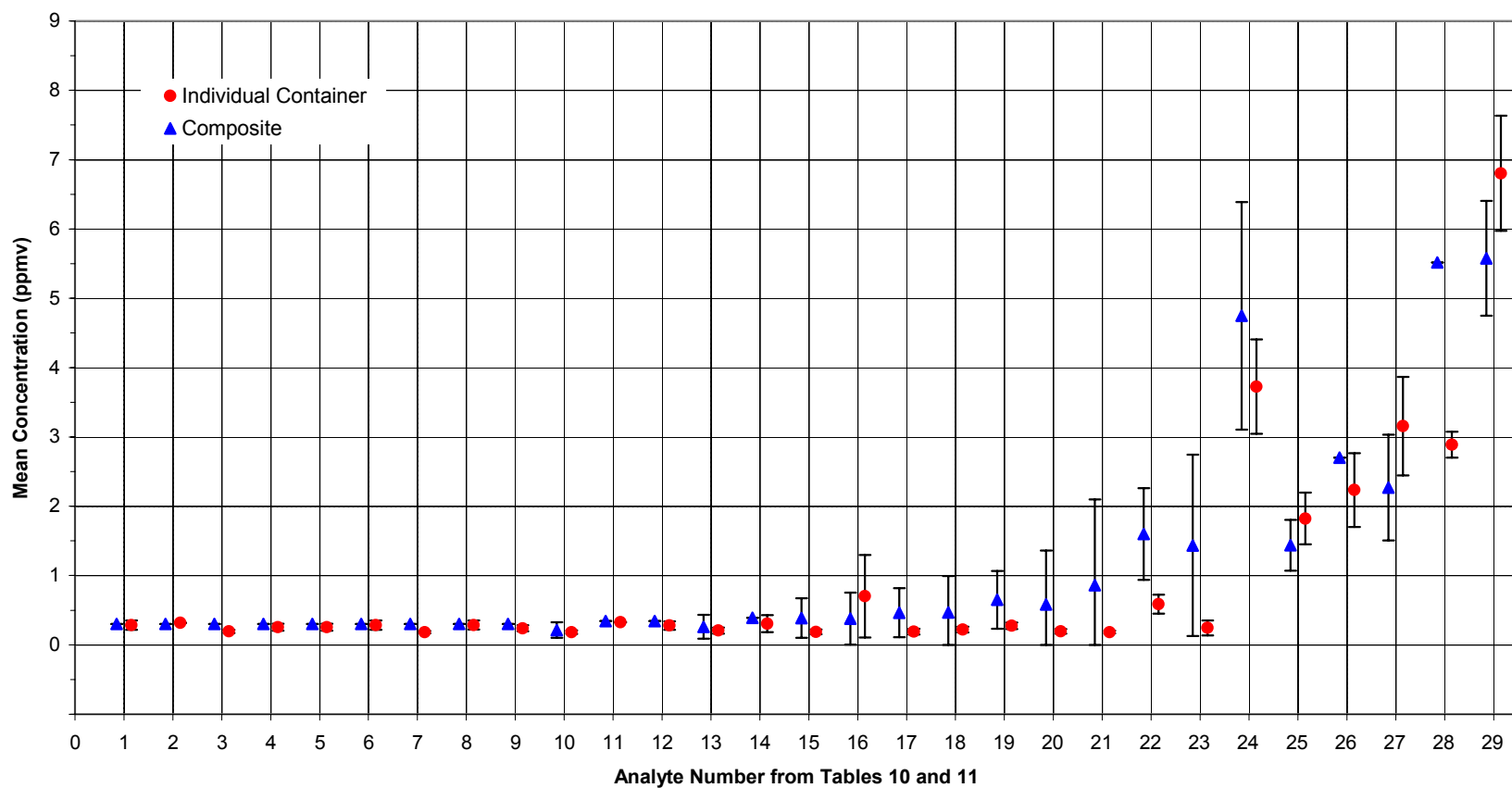


Figure 10. Mean and 90% confidence interval on the mean for 20-to-1 compositing for all analytes in RFETS waste stream

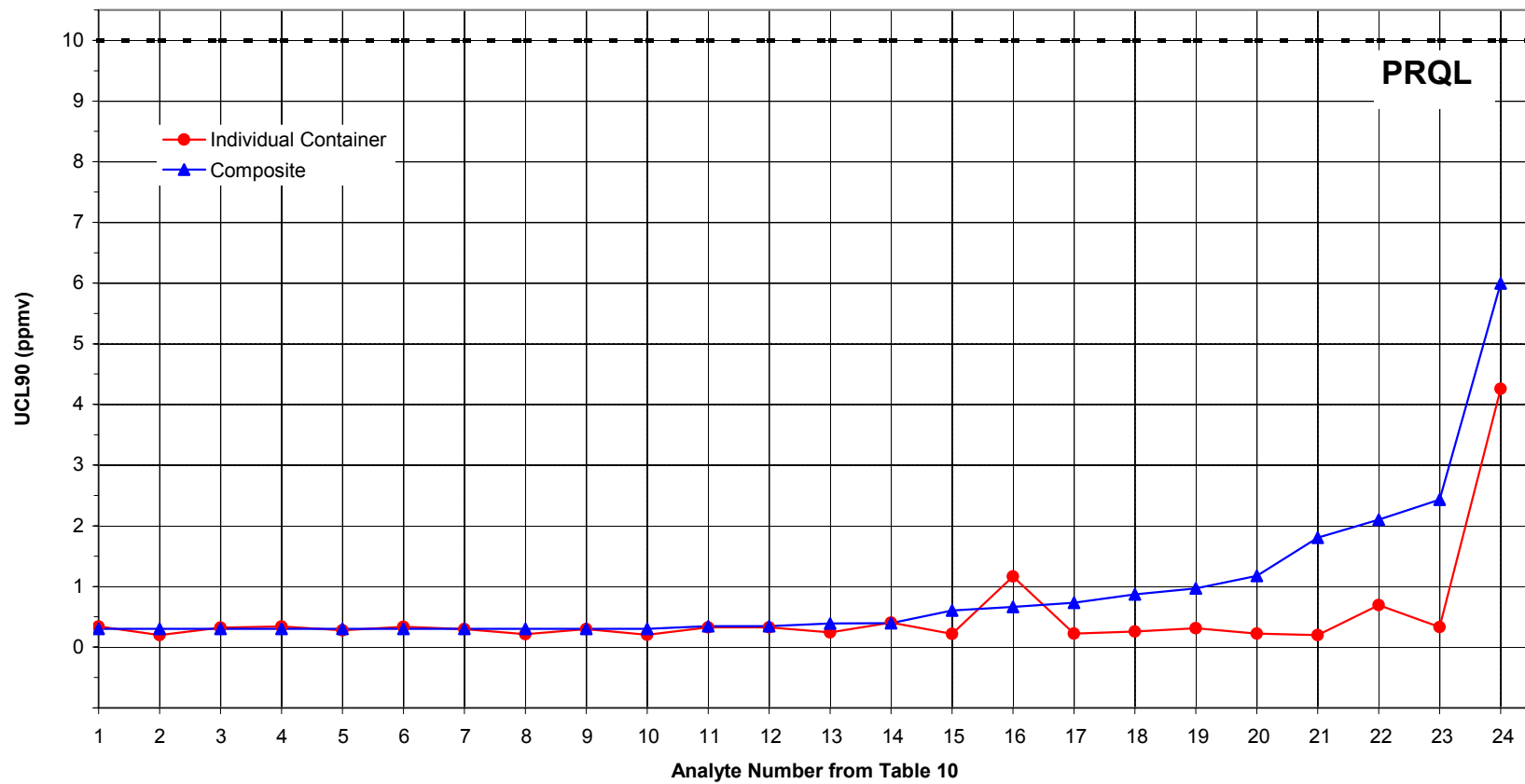


Figure 11. Upper 90% confidence limits for 20-to-1 compositing for the 10 ppmv PRQL analyte group in the RFETS waste stream

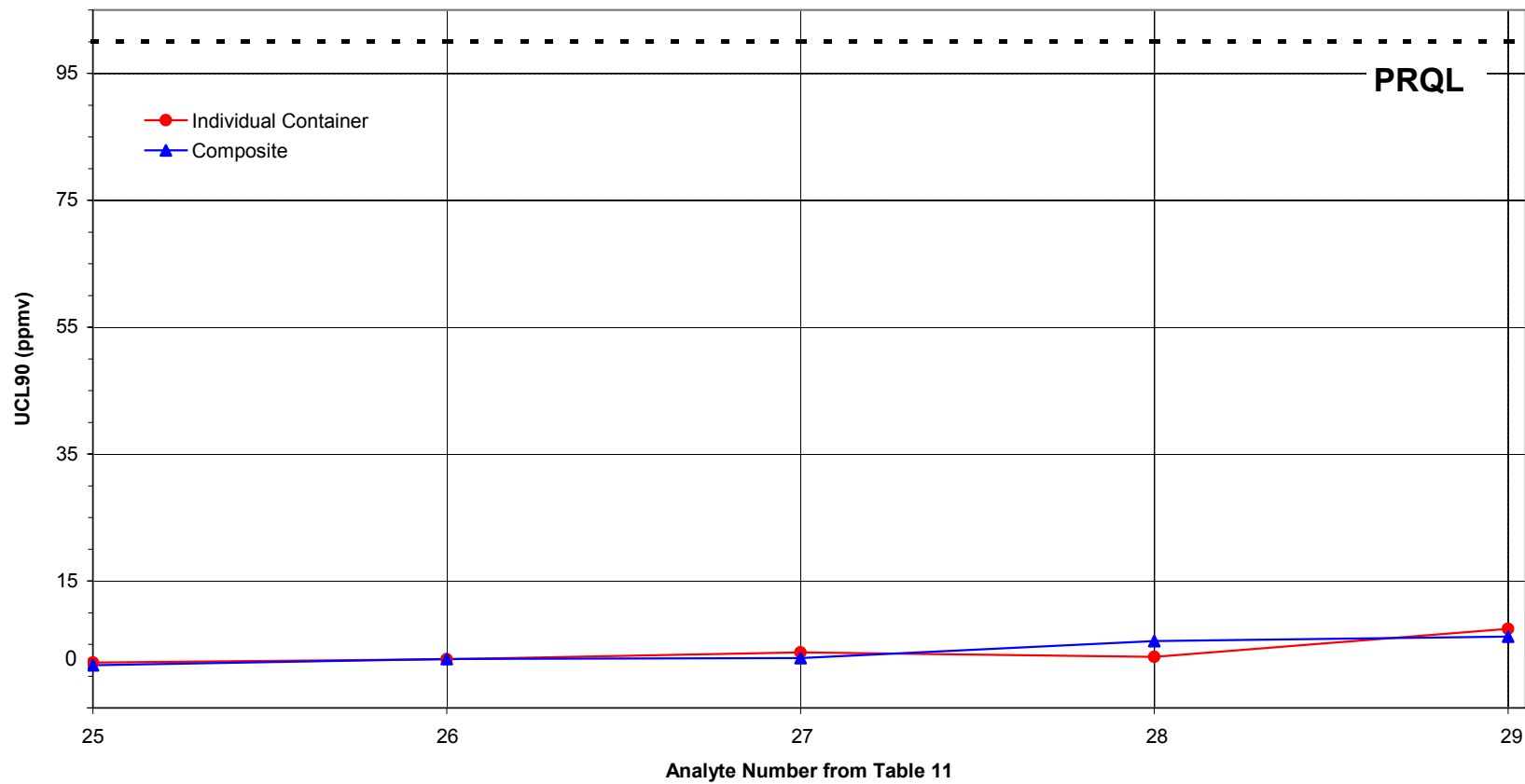


Figure 12. Upper 90% confidence limits for 20-to-1 compositing for the 100 ppmv PRQL analyte group in the RFETS waste stream

#### **2.4.4 Rocky Flats Environmental Technology Site TIC Analysis (Appendix VIII Compounds)**

For the combustible/plastic debris waste stream, there was one Appendix VIII TIC identified. Methylchloride was detected in 0.35% (4 out of 1137) of the individual container samples, well below the 25% action level. Methylchloride was not detected in the composited samples.

#### **2.4.5 Conclusion**

The headspace presented for both RFETS and INEEL support AK relative to the hazardous waste determination for those waste streams. The mean headspace concentrations for both composite and noncomposite samples have been demonstrated to have no statistical difference at the 90% confidence level. For both INEEL and RFETS, the data show that any TICs detected were well below the required action level of 25%. In addition, compositing results in  $UCL_{90}$  values that are equivalent to or more conservative than individual container sampling.



### 3. TENTATIVELY IDENTIFIED COMPOUNDS

The NMED, in their written testimony for the HWFP hearing, provides a summary statement regarding the Permit conditions for TICs that indicates three areas that are important for TIC evaluation under the WIPP program. These areas of importance are applicable to TICs that could be identified in composited HSG samples. The NMED statement is as follows:

“In summary, HSG compounds, including TICs, contained in the hazardous waste disposed at WIPP must be identified and quantified to ensure that **(1) the accuracy of hazardous waste codes assigned to a waste stream; (2) the proper characterization of waste; and (3) the protection of human health and the environment from releases of hazardous waste.** To this end, the TIC permit condition, based on SW-846 Methods and the Appendix VIII list, is both reasonable and necessary.”

The following sections describe the approach used to demonstrate the viability of composite samples in addressing the three areas of TIC importance based on the NMED written testimony.

#### 3.1 Accuracy of Hazardous Waste Codes Assigned and Proper Characterization of a Waste Stream

The WAP requires the reporting of TICs. A TIC is considered tentatively identified because the compound is not included as part of the method calibration, and therefore cannot be quantified with any degree of certainty. A TIC is added to the target analyte list if it is on the Appendix VIII list and present in 25% or more of the samples. If present in greater than 25 percent of the samples in a waste stream, the TIC must be evaluated, to determine if the TIC is a constituent of the waste. Concern has been expressed that compositing results in TICs not being resolvable as a result of dilution (i.e., they are “lost”). Given the SW-846 Method 8260 requirements, combined with the WAP-required detection limits (i.e., MDLs) this is not the case. To demonstrate this, the SW-846 Method 8260 requirements were evaluated for a typical instrument that is used in the laboratory for performing VOC analysis on a sample where 20 to 1 compositing has occurred.

In order to understand the process used to identify TICs, it is important to know how the laboratory analysis is conducted. Prior to conducting any analysis of actual samples, the analytical instrument must be calibrated to provide information on how the analytes will respond in the analytical instrument. This calibration is done for all of the target analytes that are identified as part of the program (i.e., for the WAP it is the list of analytes in Table B3-2).

Calibration is conducted using 5 different standards of known concentrations with at least one of those standards having a concentration “at or below that necessary to meet the data quality objectives of the project (Method 8260, Section 5.12.1).” The data quality objectives for headspace gas samples are the PRQLs found in Table B3-2 of the WAP. The same section of Method 8260 states that “the remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system.” In addition to the target analytes, compounds that are used for comparison to the target analytes in the actual samples are included during the calibration. These compounds are called the “internal standards” and are not present in the waste being sampled, but are chemically similar to the target analytes.

The WIPP program is designed to identify the VOC headspace gas concentrations in mixed-waste; therefore, the “range of concentrations found in typical samples” is a large range, which is regularly outside the actual calibrated range of the analytical instrument. The fact that there is a large range that falls outside the calibrated range of the instrument is demonstrated by the dilution that is regularly applied

to samples to “bring” the analytes into the calibration range. Therefore, the analytical instruments used for headspace gas analysis are calibrated throughout the “working range of the GC/MS system.”

Section 5.10 of SW-846 Method 8260 specifies that the internal standards “should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.” The 50-200% establishes how similar the internal standard must be to the target analytes and the “mid-point calibration analysis” means that the amount of internal standard used should be in the middle of the calibration range.

Understanding the calibration process and the use of the internal standard is important because the EPA convention for identifying TICs is in relation to the internal standard. Therefore, the only values that can be applied to TICs are in relation to the internal standards. To illustrate how compositing could affect the resolution of TICs, the following factors must be defined:

- The Appendix VIII TIC is present in 25% of the samples because, in order to be added to the target analyte list, it must be present at that level
- The case where 20 containers were sampled and composited for analysis is evaluated
- The analytical instrument used to process the sample is an HP5970 Mass Spectrometer (MS), this is the instrument used at the INEEL. RFETS uses HP5971 and HP5972 MSs, which are slightly newer versions of the HP5970 MS used at the INEEL.
- The calibration range for the HP5970 is 70ng to 1250 ng, which is the INEEL range. The calibration range used at the RFETS is similar.
- The EPA convention for TICs is that it have at least 10% of the nearest internal standard’s area

Because the internal standard is introduced in the middle of the calibration range, the amount of internal standard is:

$$\frac{1250 \text{ ng} - 70 \text{ ng}}{2} = 590 \text{ ng}$$

Therefore, for an individual container sample, the TIC would be present at 10% of 590 ng or 59 ng. Assuming that the TIC is present in 25% of the individual samples used in the composite sample results in the TIC being present at:

$$\frac{59 \text{ ng} * 5 \text{ samples} + 0 \text{ ng} * 15 \text{ samples}}{20 \text{ samples}} = 14.75 \text{ ng}$$

This level, 14.75 ng, is greater than the WAP’s minimum required detection level of 10 ng (WAP Table B3-2), ensuring that no TICs will be “lost” to dilution. In summary, the 20-to-1 compositing results in TICs that can be resolved at the program required detection levels (i.e., the MDL). It should be noted that this evaluation represents a conservative case scenario. Given a lower composite number (e.g., 10 to 1), higher concentrations, or higher TIC frequency (e.g., greater than 25%) resolution of TICs is also ensured. As such, the accuracy of hazardous waste codes and proper characterization of the waste is assured.

## **3.2 Protection of Human Health and the Environment**

The Permit ensures protection of human health and the environment by requiring compliance with the environmental performance standard for average VOC emissions from a disposal room. The

environmental performance standard requires meeting levels for 9 VOCs from the target analyte list. The numerical value of the performance standard was calculated based on a mathematical average concentration of the container HSG VOCs in the room. Therefore, the application of the reported HSG data is to calculate an average concentration for each of the 9 VOCs on a room basis.

The nine VOCs on the WAP-required target analyte list that are part of the environmental performance standard are:

- Carbon Tetrachloride
- Chloroform
- 1,1-Dichloroethene
- 1,2-Dichloroethane
- Methylene Chloride
- 1,1,2,2-Tetrachloroethane
- 1,1,1-Trichloroethane
- Chlorobenzene
- Toluene

These target analytes make up approximately 99% of the risk from the VOC emissions (Permit Application, Appendix D9). The NMED performed independent calculations to verify that this is the case as part of the original permitting process. The 99% risk level is based on the potential for health risk from these constituents and their prevalence in the waste. However, an additional 19 target analytes are directly measured as part of the target analyte list and provide data that can be used to provide additional protection of human health and the environment.

The Permit requires that Appendix VIII VOC TICs be reported for each container as part of the batch data report and placed on the target analyte list if they occur in greater than 25% of the containers in the waste stream. Therefore, a single TIC in an individual container does not get reported to WIPP and the waste is managed no differently because of the presence of that TIC. However, the NMED has expressed concern that the TIC information be available to “provide information in the event of a release of hazardous waste,” which is related to the requirements for the environmental performance standard.

There are 3 drivers for the WIPP environmental performance standard: 1) the potential for long term exposure at the surface, 2) exposure to a worker under an immediately dangerous to life and health (IDLH) concentration in the underground, 3) the lower explosive limit (LEL). These drivers apply to the actual limits for the 9 VOCs that are part of the environmental performance standard and are not directly related to any requirements for TICs. However, these drivers provide context for evaluating the potential effect of TICs on human health and the environment.

The 9 specified constituents in the environmental performance standard (i.e., listed in HWFP Table IV.D.1) comprise 99% of the risk, therefore, the contribution from a single TIC in an individual container does not affect this 99% risk level. This is because the only way that a TIC could affect this risk level is for it to be present in 25% of the samples, be added to a target analyte list, and subsequently added to the list of specified constituents required for the VOC monitoring program. Therefore, the only hazard that could be present due to a single TIC in an individual container would be from an immediate hazard.

A single TIC in an individual container may have the potential for an immediate hazard to a worker by being at IDLH or LEL concentration. This immediate hazard would be related to the NMED statement that the TIC information be available to “provide information in the event of a release of hazardous waste.” The lowest IDLH is less than the LEL concentration; therefore, it is bounding. The lowest IDLH

for the VOCs on the Appendix VIII list is 2 ppmv for acrolein. It is important to note that acrolein has not been identified in transuranic (TRU) waste and is considered here solely because it is on the Appendix VIII list and represents the lowest IDLH.

Assuming a molecular weight and analytical response equivalent to carbon tetrachloride, it can be shown that compositing allows for detection of constituents that exceed IDLH levels in a single drum at a location where workers are present. Carbon tetrachloride exhibits an analytical response that is typical of VOCs, and is therefore appropriate for this calculation.

In order to compare the acrolein ppmv concentration to what is required by the WAP, a target analyte must be chosen for the comparison. Carbon tetrachloride is a typical analyte that falls in the middle of the range of the target analytes in terms of its response on the analytical instruments. For carbon tetrachloride, the detection required by the WAP is 0.16 ppmv converted from the 10 ng in 10 mL requirement in Table B3-2 using the ideal gas law. For a single TIC in an individual container out of a composite group of 20, the detection level would be  $0.16 * 20 = 3.2$  ppmv, where 20 is the dilution factor for only 1 container out of the 20 containers with the TIC. For compositing samples at 10 to one, the detection level is 1.6 ppmv and for 5 to 1 it is 0.8 ppmv. These concentrations are what are measurable in the drum headspace.

The concentration of concern is that concentration to which a worker could be exposed in an event involving a release. In a diffusion driven system, a plume can be modeled as an expanding hemisphere, as is common industrial hygiene practice. The concentration at a distance,  $r$ , from the source is found using the following equation:

$$\frac{C_1}{Cr} = \frac{Vr}{V_1}$$

where:

$C_1$  = source concentration in ppmv

$C_r$  = concentration at a point away from the source

$V_1$  = initial volume of the source (conservatively assumed to be the volume of a drum =  $0.2 \text{ m}^3$ )

$V_r$  = volume of a hemisphere of radius  $r = \frac{2}{3}\pi r^3$

Using this relationship, at approximately 0.53 meters from the source, the concentration is less than the IDLH when the source concentration is at the detection limit of 3.2 ppmv. Thus, even without mine ventilation, a worker would have to be closer than 0.53 meters to the drum to receive an IDLH dose for this extreme case. Airflow (typically greater than 70,000 cubic feet per minute in a disposal room) will further dilute the release. This analysis shows, that even for the extreme case, TICs in composite samples up to 20 to 1 can be identified at a level that assures protection of human health and the environment.

## **4. SUMMARY**

Compositing is a physical averaging of HSG that yields WAP compliant data. The mean has been demonstrated to be equivalent for both compositing and non-compositing results. The composited  $UCL_{90}$  values have been demonstrated to be equivalent to or more conservative than individual container results. Compositing yields TIC data that meets WAP requirement for a waste stream characterization and is protective of human health and the environment. TICs that have been observed are well below the 25% frequency for both composited and individual container results. Potential TICs that are present at a level that could affect human health and the environment are detectable in composite samples.

**Attachment C**  
**INFORMATION SUPPORTING ITEM 2**

**JOINT NRC/EPA GUIDANCE DOCUMENT AND DOE ORDERS RELATED TO THE  
IMPLEMENTATION OF RADIATION SAFETY**

**VE HAZARDS DOCUMENTATION FROM THE ROCKY FLATS ENVIRONMENTAL  
TECHNOLOGY SITE**

**JOINT NRC/EPA GUIDANCE DOCUMENT AND DOE ORDERS RELATED TO THE  
IMPLEMENTATION OF RADIATION SAFETY**

discussions with representatives of the NRC staff regarding proposed final SRP Chapter 19, Regulatory Guide DG-1061, and use of uncertainty versus point values in the PRA-related decisionmaking process.

**10:15 A.M.–12:00 Noon: Operating Events at Oconee Nuclear Power Plant Units 1 and 2 (Open)**—The Committee will hear presentations by and hold discussions with representatives of the NRC staff regarding the results of the investigation performed by an Augmented Inspection Team (AIT) of the June 20 and 23 event at Oconee Unit 1 involving failure of emergency electrical power supply, and of the April 22, 1997 event at Oconee Unit 2 that involved inoperability of the high pressure injection pump.

**1:00 P.M.–3:00 P.M.: Capability and Application of the EPRI Checkworks Code (Open)**—The Committee will hear presentations by and hold discussions with representatives of the NRC staff and Electric Power Research Institute (EPRI) regarding the capability and application of the EPRI Checkworks Code.

**3:15 P.M.–3:45 P.M.: Future ACRS Activities (Open)**—The Committee will discuss the recommendations of the Planning and Procedures Subcommittee regarding items proposed for consideration by the full Committee during future meetings.

**3:45 P.M.–4:00 P.M.: Reconciliation of ACRS Comments and Recommendations (Open)**—The Committee will discuss responses from the NRC Executive Director for Operations (EDO) to comments and recommendations included in recent ACRS reports, including the EDO response to the October 10, 1997 ACRS report related to the differing professional opinion pertaining to steam generator tube integrity.

**4:00 P.M.–4:15 P.M.: Election of ACRS Officers For CY 1998 (Open)**—The Committee will elect the Chairman and Vice Chairman for the ACRS, and Member-at-Large for the Planning and Procedures Subcommittee for CY 1998.

**4:15 P.M.–7:00 P.M.: Preparation of ACRS Reports (Open)**—The Committee will continue its discussion of proposed ACRS reports on matters considered during this meeting.

#### Saturday, December 6, 1997

**8:30 A.M.–9:00 A.M.: Report of the Planning and Procedures**

**Subcommittee (Open/Closed)**—The Committee will hear a report of the Planning and Procedures Subcommittee on matters related to the conduct of ACRS business, qualifications of candidates nominated for appointment to the ACRS, agenda for the planning meeting, and organizational and personnel matters relating to the ACRS.

[Note: A portion of this session may be closed to discuss organizational and personnel matters that relate solely to the internal personnel rules and practices of this Advisory Committee, and information the release of which would constitute a clearly unwarranted invasion of personal privacy.]

**9:00 A.M.–4:00 P.M. (12:00–1:00 P.M. Lunch): Preparation of ACRS Reports (Open)**—The Committee will continue its discussion of proposed ACRS reports on matters considered during this meeting.

**4:00 P.M.–4:30 P.M.: Miscellaneous (Open)**—The Committee will discuss matters related to the conduct of Committee activities and matters and specific issues that were not completed during previous meetings, as time and availability of information permit.

Procedures for the conduct of and participation in ACRS meetings were published in the **Federal Register** on September 4, 1997 (62 FR 46782). In accordance with these procedures, oral or written views may be presented by members of the public, including representatives of the nuclear industry, electronic recordings will be permitted only during the open portions of the meeting, and questions may be asked only by members of the Committee, its consultants, and staff. Persons desiring to make oral statements should notify Mr. Sam Duraiswamy, Chief, Nuclear Reactors Branch, at least five days before the meeting, if possible, so that appropriate arrangements can be made to allow the necessary time during the meeting for such statements. Use of still, motion picture, and television cameras during this meeting may be limited to selected portions of the meeting as determined by the Chairman. Information regarding the time to be set aside for this purpose may be obtained by contacting the Chief of the Nuclear Reactors Branch prior to the meeting. In view of the possibility that the schedule for ACRS meetings may be adjusted by the Chairman as necessary to facilitate the conduct of the meeting, persons planning to attend should check with the Chief of the Nuclear Reactors Branch if such rescheduling would result in major inconvenience.

In accordance with Subsection 10(d) P.L. 92–463, I have determined that it is necessary to close portions of this meeting noted above to discuss matters that relate solely to the internal personnel rules and practices of this Advisory Committee per 5 U.S.C. 552b(c)(2) and to discuss information the release of which would constitute a clearly unwarranted invasion of personal privacy per 5 U.S.C. 552b(c)(6).

Further information regarding topics to be discussed, whether the meeting has been canceled or rescheduled, the Chairman's ruling on requests for the opportunity to present oral statements and the time allotted therefor, can be obtained by contacting Mr. Sam Duraiswamy, Chief, Nuclear Reactors Branch (telephone 301/415-7364), between 7:30 A.M. and 4:15 P.M. EST.

ACRS meeting agenda, meeting transcripts, and letter reports are available for downloading or reviewing on the internet at <http://www.nrc.gov/ACRSACNW>.

The ACRS meeting dates for Calendar Year 1998 are provided below:

ACRS Meeting No.	1998 ACRS Meeting Date
448 .....	Jan.—No Meeting.
449 .....	Feb. 5–7, 1998.
450 .....	Mar. 2–4, 1998.
	Mar. 5–7, 1998.
	(Safety Research Program)
451 .....	Apr. 2–4, 1998.
452 .....	Apr. 30–May 2, 1998.
453 .....	June 3–5, 1998.
454 .....	July 8–10, 1998.
	Aug.—No Meeting.
455 .....	Sept. 2–4, 1998.
456 .....	Oct. 1–3, 1998.
457 .....	Nov. 5–7, 1998.
458 .....	Dec. 3–5, 1998.

Dated: November 14, 1997.

**Andrew L. Bates,**

*Advisory Committee Management Officer.*

[FR Doc. 97–30526 Filed 11–19–97; 8:45 am]

BILLING CODE 7590–01–P

## NUCLEAR REGULATORY COMMISSION

### ENVIRONMENTAL PROTECTION AGENCY

#### Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste

**AGENCIES:** Environmental Protection Agency and Nuclear Regulatory Commission.

**ACTION:** Publication of Final Joint Guidance on the Testing Requirements for Mixed Waste.



**SUMMARY:** The Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA) are jointly publishing herein final guidance on the testing requirements for mixed radioactive and hazardous waste (mixed waste). NRC and EPA began development of this guidance in 1987 and a draft was completed in 1989. EPA's adoption of the Toxicity Characteristic Leaching Procedure (TCLP) in 1990 required the agencies to substantially revise the guidance. The agencies issued a draft for public comment on March 26, 1992. A public meeting was held on April 14, 1992, in Washington, D.C., to solicit oral comments on the draft guidance document. The comment period ended on May 26, 1992. NRC and EPA received more than 700 requests for copies of the draft guidance document and NRC received approximately 100 written comments from 20 individuals and groups, including comments resulting from a review of the guidance by the U.S. Department of Energy. NRC and EPA staffs have incorporated the appropriate comments into the final guidance.

The guidance emphasizes the use of process knowledge, whenever possible, to determine if a waste is hazardous as a way to avoid unnecessary exposures to radioactivity. The guidance also provides guidelines for generators wishing to rely on process knowledge as the basis for evaluating their waste.

The guidance offers two strategies for helping to maintain radiation exposures As Low As is Reasonably Achievable (ALARA) if testing is required. These strategies are the use of a sample size of less than 100 grams, as long as the resulting test is sufficiently sensitive to measure the constituents of interest at the regulatory levels prescribed in the TCLP, and the use of surrogate materials, as long as they are chemically identical to the mixed waste and faithfully represent the hazardous constituents in the waste mixture.

The guidance also discusses other allowable sampling and testing procedures, such as representative drum sampling, or sampling from drums containing lower concentrations of radioactive material, as long as the chemical contents are identical to those found in the drums with higher concentrations of radioactive material.

**FOR FURTHER INFORMATION CONTACT:** Dominick A. Orlando, Division of Waste Management, Office of Nuclear Material Safety and Safeguards, U.S. Nuclear Regulatory Commission, Washington, D.C., 20555, telephone (301) 415-6749 or Newman Smith, Permits and State

Programs Division, Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C., 20460, telephone (703) 308-8757.

Dated at Rockville, MD and Washington, DC this 7th day of November, 1997.

For the U.S. Nuclear Regulatory Commission.

**Carl J. Paperiello,**

*Director, Office of Nuclear Material Safety and Safeguards.*

For the U.S. Environmental Protection Agency.

**Elizabeth Cotsworth,**

*Acting Director, Office of Solid Waste.*

#### SUPPLEMENTARY INFORMATION:

#### Clarification of RCRA Hazardous Waste Testing Requirements for Low-Level Radioactive Mixed Waste—Final Guidance

*Disclaimer:* The policies discussed in this document are not final Agency actions, but are intended solely as guidance. They are not intended, nor can they be relied upon, to create any rights enforceable by any party in litigation with the United States. The Environmental Protection Agency and Nuclear Regulatory Commission may follow the guidance, or act at variance with the guidance, based on an analysis of specific site circumstances. The agencies also reserve the right to change the guidance at any time, without public notice.

#### ACRONYMS/ABBREVIATIONS USED IN THIS GUIDANCE

Acronym/abbreviation	Definition
AEA .....	Atomic Energy Act.
ALARA .....	As Low As Is Reasonably Achievable.
BDAT ....	Best Demonstrated Available Technology.
CFR .....	Code of Federal Regulations.
EP .....	Extraction Procedure (toxicity test).
EPA .....	Environmental Protection Agency.
FR .....	Federal Register.
HSWA ..	Hazardous and Solid Waste Amendments.
LDR .....	Land Disposal Restrictions.
NRC .....	Nuclear Regulatory Commission.
OSWER ..	Office of Solid Waste and Emergency Response.
RCRA ...	Resource Conservation and Recovery Act.
SW-846 ..	Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods.
TC .....	Toxicity Characteristic.
TCLP ....	Toxicity Characteristic Leaching Procedure.
TSDF ....	Treatment, Storage or Disposal Facility.
WAP .....	Waste Analysis Plan.

#### I. Background

Mixed waste is defined as waste that contains both hazardous waste subject to the requirements of the Resource Conservation and Recovery Act (RCRA) and source, special nuclear, or by-product material subject to the requirements of the Atomic Energy Act (AEA).<sup>1</sup> This guidance addresses testing activities related to mixed low-level waste (LLW), which is a subset of mixed waste.<sup>2</sup> The term "mixed waste," for the purposes of this document, will refer to mixed LLW. Additional information on the testing of hazardous wastes, which could apply to both mixed LLW and other types of mixed waste (e.g., high-level and transuranic mixed waste), is found in Appendix A. The information below is intended for use by Nuclear Regulatory Commission (NRC) licensees that may not be familiar with the hazardous waste characterization and testing requirements that apply to mixed waste. The guidance assumes that the reader is familiar with the NRC's regulations and regulatory framework for the management of radioactive material and focuses on compliance with the Environmental Protection Agency's (EPA's) requirements for the management of hazardous waste. Although it is written for commercial mixed waste generators, the guidance may also be useful for Federal facilities that generate mixed waste.

Users of this guidance should have a good understanding of how mixed waste is defined (see above), and what authority, or authorities, regulate mixed waste testing activities. The hazardous component of mixed waste is regulated by EPA in those States where EPA implements the entire RCRA Subtitle C hazardous waste program (i.e., unauthorized States). Currently, EPA regulates mixed waste in Alaska, Hawaii, Iowa, Puerto Rico, the Virgin Islands, and American Samoa. In most instances mixed waste is regulated by State governments. Thirty-nine States and one territory (Guam) have been delegated authority by EPA to implement the base RCRA hazardous waste program and to regulate mixed waste activities (see 51 FR 24504, July 3, 1986, and Appendix B). These States are referred to as "mixed waste authorized States." Nine additional States are authorized for the RCRA base hazardous waste program but have not been delegated authority by EPA to

<sup>1</sup> See 42 U.S.C. § 6903 (41), added by the Federal Facility Compliance Act of 1992 (FFCA).

<sup>2</sup> See revised *Guidance on the Definition and Identification of Commercial Low-Level Radioactive and Hazardous Waste and Answers to Anticipated Questions*, October 4, 1989.

regulate mixed waste.<sup>3</sup> In these States mixed waste is not regulated by EPA, but may be regulated by States under the authority of State law. It is important that licensees contact the State hazardous waste agencies in authorized States to determine the specific testing, analysis, and other hazardous waste requirements that may apply to mixed waste managed in their State, because their State may have more stringent requirements than the Federal requirements discussed in this guidance.

This guidance describes:

- (1) The current regulatory requirements for determining if a waste is a RCRA hazardous waste;
- (2) The role of waste knowledge for hazardous waste determinations;
- (3) The waste analysis information necessary for proper treatment, storage, and disposal of mixed waste; and,
- (4) The implications of the RCRA land disposal restrictions (LDRs) on the waste characterization and analysis requirements.

This information should be useful for: (1) radioactive waste generators, who must determine if their waste is a RCRA hazardous waste, and therefore a mixed waste; (2) for those generators storing mixed waste on-site in tanks, containers or containment buildings for longer than 90 days, that consequently become responsible for complying with RCRA and NRC storage requirements; and (3) those facilities that accept mixed waste for off-site treatment, storage, or disposal.

Generators and/or treatment, storage, and disposal facilities (TSDFs) handling wastes under RCRA must characterize their waste for several purposes:

- (1) To determine if their waste is a hazardous waste (40 CFR 262.11);
- (2) To comply with general waste analysis requirements for new or permitted TSDFs, for TSDFs operating under interim status, and for certain generators that treat land disposal prohibited wastes in 40 CFR 264.13, 265.13 and 268.7, respectively. These analysis requirements include:
  - (a) chemical/physical analysis of a representative sample (and/or, in some cases, use waste knowledge (see below); and,
  - (b) preparation of a waste analysis plan.
- (3) To meet the waste analysis requirements that apply to the specific

waste management methods in 40 CFR 264.17, 264.314, 264.341, 264.1034(d), and 268.7;

- (4) To ensure, prior to land disposal, that the restricted waste meets the required treatment standard (40 CFR 268.7).<sup>4</sup>

This guidance addresses the need for chemical analysis of mixed wastes to meet these purposes. The guidance also emphasizes ways in which unnecessary testing of mixed waste may be avoided. This is important when handling mixed waste, since each sampling, workup, or analytical event may involve an incremental exposure to radiation. This guidance encourages mixed waste handlers to use waste knowledge, such as process knowledge, where possible, in making RCRA hazardous waste determinations involving mixed waste. It also encourages the elimination of redundant testing by off-site treatment and disposal facilities, where valid generator-supplied, and certified, data are available.

Because mixed waste testing may pose the possibility of increased radiation exposures, this guidance also describes methods by which individuals who analyze mixed waste samples may reduce their occupational radiation exposure and satisfy the intent of the RCRA testing requirements. Testing to determine whether wastes are hazardous under the RCRA toxicity characteristic may pose special concerns which are examined in Section III of this guidance.

All of the activities described in this guidance are subject to the requirements of both the AEA and RCRA. The focus of this guidance is the RCRA requirements. NRC and NRC Agreement State licensees are authorized to receive, possess, use (which includes storing, sampling, testing, and treating), and dispose of AEA-licensed materials. NRC licensees handling mixed waste should ensure that their RCRA hazardous waste testing activities are consistent with NRC, or Agreement State, regulations and license conditions. Flexibility in the RCRA requirements is emphasized so that the As Low As is Reasonably Achievable (ALARA) concept can be incorporated into the mixed waste testing activities.<sup>5</sup> If other AEA requirements, or RCRA requirements are difficult to meet in a specific mixed waste management situation, licensees should seek resolution by requesting license amendments, approval of

modifications to their RCRA permits or interim status Part A applications, or resolution under both authorities.

Section 1006(a) of RCRA states "Nothing in this Act shall be construed to apply to (or authorize any State, interstate, or local authority to regulate) any activity or substance which is subject to \* \* \* the Atomic Energy Act of 1954 \* \* \* except to the extent that such application (or regulation) is not inconsistent with the requirements of such Acts." If a resolution cannot be achieved through the flexibility provided by the two regulatory frameworks, then and only then, should licensees seek resolution under Section 1006(a) of RCRA. Licensees should note that, if an inconsistency exists, relief will be limited to that specific RCRA requirement, and that the determination of an inconsistency would not relieve the licensee from all other RCRA requirements. Section 1006(a) and radiological hazard considerations are addressed more fully in Sections III and IV of this guidance. NRC licensees should also include the necessary flexibility in their RCRA permit waste analysis plans to accommodate the sampling and testing required to meet AEA requirements.

## II. Use of Waste Knowledge for Hazardous Waste Determinations

The use of waste knowledge by a generator and/or a TSDF to characterize mixed waste is recommended throughout this document to eliminate unnecessary or redundant waste testing. EPA interprets "waste knowledge" or "acceptable knowledge" of a waste broadly to include, where appropriate:

- "Process knowledge";
- Records of analyses performed by generator or TSDF prior to the effective date of RCRA regulations; or,
- A combination of the above information, supplemented with chemical analysis.

Process knowledge refers to detailed information on processes that generate wastes subject to characterization, or to detailed information (e.g., waste analysis data or studies) on wastes generated from processes similar to that which generated the original waste. Process knowledge includes, for example, waste analysis data obtained by TSDFs from the specific generators that sent the waste off-site, and waste analysis data obtained by generators or TSDFs from other generators, TSDFs or areas within a facility that test chemically identical wastes.<sup>6</sup>

<sup>3</sup> The RCRA base hazardous waste program is the RCRA program initially made available for final authorization and includes Federal regulations up to July 26, 1982. However, authorized States have revised their programs to keep pace with Federal program changes that have taken place after 1982 in accordance with EPA regulation.

<sup>4</sup> Refer to Appendix A for specific EPA regulations pertaining to (1)-(4).

<sup>5</sup> ALARA, codified in 10 CFR Part 20, refers to the practice of maintaining all radiation exposures, to workers and the general public, as low as is reasonably achievable.

<sup>6</sup> For a more detailed discussion on process knowledge, see Section 1.5 in "Waste Analysis at

Waste knowledge is allowed by RCRA regulations for the following hazardous waste characterization determinations:

- To determine if a waste is characteristically hazardous (40 CFR 262.11(c)(2)) or matches a RCRA listing in 40 CFR Part 261, Subpart D (40 CFR 262.11(a) and (b));
- To comply with the requirement to obtain a detailed chemical/physical analysis of a representative sample of the waste under 40 CFR 264.13(a);
- To determine whether a hazardous waste is restricted from land disposal (40 CFR 268.7(a)); and,
- To determine if a restricted waste the generator is managing can be land disposed without further treatment (see the generator certification in 40 CFR 268.7(a)(3) and information to support the waste knowledge determination in 40 CFR 268.7(a)(6)).

Hazardous waste, including mixed waste, may be characterized by waste knowledge alone, by sampling and laboratory analysis, or a combination of waste knowledge, and sampling and laboratory analysis. The use of waste knowledge alone is appropriate for wastes that have physical properties that are not conducive to taking a laboratory sample or performing laboratory analysis. As such, the use of waste knowledge alone may be the most appropriate method to characterize mixed waste streams where increased radiation exposures are a concern. Mixed waste generators should contact the appropriate EPA regional office to determine whether they possess adequate waste knowledge to characterize their mixed waste.

### III. Determinations by Generators That a Waste Is Hazardous

A solid waste is a RCRA hazardous waste if it meets one of two conditions: (1) the waste is specifically "listed" in 40 CFR Part 261, Subpart D, or; (2) the waste exhibits one of the four "characteristics" identified in 40 CFR Part 261, Subpart C. These characteristics are:

- Ignitability;
- Corrosivity;
- Reactivity; or,
- Toxicity.

#### (a) Listed Hazardous Wastes

Generators of waste containing a radioactive and solid waste component must establish whether the solid waste component is a RCRA hazardous waste. Determinations of whether a waste is a listed hazardous waste can be made by

comparing information on the waste stream origin with the RCRA listings set forth in 40 CFR Part 261, Subpart D. These listings are separated into three major categories or lists, and are identified by EPA hazardous waste numbers. Most hazardous waste numbers are associated with a specific waste description, specific processes that produce wastes, or certain chemical compounds. For example, K103 waste is defined as "process residues from aniline extraction from the production of aniline." A generator who produces such residues should know, without any sampling or analysis, that these wastes are "listed" RCRA hazardous wastes by examining the K103 hazardous waste description in the hazardous waste lists. Other hazardous waste numbers describe wastes generated from generic processes that are common to various industries and activities. These wastes are referred to as hazardous wastes from nonspecific sources. Radioactively contaminated spent solvents are the most likely mixed wastes to be nonspecific source listed wastes. For example, a generator using one of the F002 halogenated solvents (e.g., tetrachloroethylene, trichloroethylene, and chlorobenzene, etc.) to remove paint from a radiologically contaminated surface, can determine that this waste is a listed RCRA hazardous waste by examining the F002 waste definition for the solvent type, and for a solvent mixture/blend, the percent solvent by volume.

In addition to wastes that are specifically listed as hazardous, the "derived from" and "mixture" rules state that any solid waste derived from the treatment, storage, or disposal of a listed RCRA hazardous waste, or any solid waste mixed with a listed RCRA hazardous waste, respectively, is itself a listed RCRA hazardous waste until delisted (see 40 CFR 261.3).<sup>7</sup> (Note that soil and debris can be managed as hazardous wastes if they contain listed hazardous wastes or they exhibit one or more hazardous waste characteristics. See hazardous debris definition in 40 CFR 268.2.)

<sup>7</sup>The "mixture" and "derived-from" rules were vacated and remanded due to EPA's failure to provide adequate notice and opportunity for comment before their 1980 promulgation, in *Shell Oil v. EPA*, No. 80-1532 (D.C. Cir. Dec. 6, 1991). At the Court's suggestion, EPA reinstated the "mixture" and "derived-from" rules as interim final until the rules are revised through new EPA rulemaking. The "mixture" and "derived from" rules adopted by those States with authorized RCRA programs were not affected by the court case or the subsequent reinstatement by EPA. For further information, see 57 FR 49278, October 30, 1992, and 60 FR 66344, December 21, 1995.

Exceptions to the "mixture rule" and "derived from" rules exist for certain solid wastes. For example, wastewater discharges subject to Clean Water Act permits, under certain circumstances, are not RCRA hazardous (see 40 CFR 261.3(a)(2)(iv)). Also, hazardous wastes which are listed solely for a characteristic identified in Subpart C of 40 CFR Part 261 (e.g., a F003 spent solvent which is listed only because it is ignitable) are not considered hazardous wastes when they are mixed with a solid waste and the resultant mixture no longer exhibits any characteristic of a hazardous waste (see 40 CFR 261.3(a)(2)(iii)). Likewise, waste pickle liquor sludge "derived from" the lime stabilization of spent pickle liquor (e.g., K062) is not a RCRA listed hazardous waste, if the sludge does not exhibit a hazardous waste characteristic (see discussion below on characteristic hazardous wastes). It should be noted, however, that wastes such as F003 and K062 *must* meet LDR treatment standards. Outside of the exceptions mentioned here and in the RCRA regulations, a hazardous waste that was generated via the "mixture rule" or the "derived from" rule must be delisted through a specific EPA petition process for the listed waste to be considered only a solid waste, and no longer managed as a listed hazardous waste under the RCRA Subtitle C system.

When applying the mixture rule to hazardous wastes, including mixed wastes, generators should be aware that EPA prohibits the dilution (i.e., mixing) of land disposal restricted waste or treatment residuals as a substitute for adequate treatment (see 40 CFR 268.3). An exception to the prohibition is the dilution of purely corrosive, and in some cases, reactive, or ignitable non-toxic wastes to eliminate the characteristic, or the aggregation of characteristic wastes in (pre)treatment systems regulated under the Clean Water Act (55 FR 22665).

#### (b) Characteristic Hazardous Wastes

Hazardous characteristics are based on the physical/chemical properties of wastes. Thus, physical/chemical testing of waste may be appropriate for determining whether a waste is a characteristic hazardous waste. *RCRA regulations, however, do not require testing. Rather, generators must determine whether the waste is a RCRA hazardous waste.* Such a determination may be made based on one's knowledge of the materials or chemical processes that were used. EPA's regulations are clear on this point. 40 CFR 262.11(c) states:

“ . . . if the waste is not listed [as hazardous waste] in Subpart D [of 40 CFR Part 261], the generator must then determine whether the waste is identified in Subpart C of 40 CFR Part 261 by either:

(1) Testing the waste according to the methods set forth in Subpart C of 40 CFR Part 261, or according to an equivalent method approved by the Administrator under 40 CFR 260.21; or

(2) Applying knowledge (emphasis added) of the hazardous characteristic of the waste in light of the materials or the processes used.”

Therefore, where sufficient material or process knowledge exists, the generator need not test the waste to make a hazardous characteristic determination, although generators and subsequent handlers would be in violation of RCRA, if they managed hazardous waste erroneously classified as non-hazardous, outside of the RCRA hazardous waste system. For this reason, facilities wishing to minimize testing often assume a questionable waste is hazardous and handle it accordingly.

A generator must also comply with the land disposal restriction regulations in 40 CFR 268 which require the generator to determine whether the waste is prohibited from land disposal (refer to Section V for a detailed discussion of these requirements).<sup>8</sup> With respect to the hazardous characteristic, and the determination as to whether a waste is restricted from land disposal under 40 CFR 268.7(a), a generator may select the option of using waste knowledge. However, if the waste is determined to be land disposal restricted in 40 CFR 268.7(a), some testing will generally be required prior to land disposal, except where technologies are specified as the treatment standard. For mixed waste, EPA recommends that the frequency of such testing be held to a minimum, in order to avoid duplicative testing and repeated exposure to radiation.

In determining whether a radioactive waste is a RCRA hazardous waste, the generator may test a surrogate material (i.e., a chemically identical material with significantly less or no

radioactivity) to determine the RCRA status of the radioactive waste. This substitution of a surrogate material may either partially or completely supplant the testing of the waste. A surrogate material, however, should only be used if the surrogate material faithfully represents the hazardous constituents of the mixed waste.<sup>9</sup> The following example discusses the use of surrogates. A generator is required to determine if a process waste stream containing lead (D008) exceeds the regulatory level of 5.0 milligrams per liter for the toxicity characteristic (40 CFR 261.24). If this determination cannot be made based on material and process knowledge only, the generator would need to test the hazardous material. Rather than testing the radioactive waste stream, the generator may opt to test a surrogate or chemically identical non-radioactive, or lower activity, radioactive waste stream generated by similar maintenance activities in another part of the plant. This substitution of materials is acceptable as long as the surrogate material faithfully represents the characteristics of the actual waste, and testing provides sufficient information for the generator to reasonably determine if the waste is hazardous under RCRA. Non-radioactive or lower activity quality control samples/species and spiked solutions, for instance, are acceptable to minimize exposure to radiation from duplicative mixed waste testing.

As part of the hazardous waste determination, a generator must document test results or other data and methods that it used. Specifically, 40 CFR 262.40(c) states that “a generator must keep records of any test results, waste analyses, or other determinations made in accordance with 40 CFR 262.11 for at least three years from the date that the waste was last sent to on-site or off-site treatment, storage, or disposal.” Section V of this guidance contains information on record keeping requirements for land disposal restricted hazardous (and mixed) wastes.

In summary, testing listed wastes to make the hazardous waste determination is not necessary, because most RCRA hazardous waste codes or listings identify specific waste streams from specific processes or specific categories of wastes. Testing will most often occur to determine if a waste exhibits a hazardous characteristic. However, testing is not required if a

generator has sufficient knowledge about the waste and its physical/chemical properties to determine that it is non-hazardous.<sup>10</sup> It is recognized that certain mixed waste streams, such as wastes from remediation activities or wastes produced many years ago, may have to be identified using laboratory analysis, because of a lack of waste or process information on these waste streams. Nonetheless, hazardous waste determinations based on generator knowledge can be used to reduce the sampling of mixed waste and prevent unnecessary exposure to radioactivity. The same principle holds for a generator's determination that a waste is subject to the RCRA land disposal restrictions in 40 CFR 268.7(a).

#### IV. Testing Protocols for Characteristics

When testing is conducted to determine whether a waste is a RCRA hazardous waste, there are acceptable test protocols or criteria for each of the four characteristics. Testing for characteristics must be done on a representative sample of the waste or using any applicable sampling methods specified in Appendix I of 40 CFR 261.<sup>11</sup>

**Ignitability**—For liquid wastes, other than aqueous solutions containing by volume less than 24 percent alcohol, the flash point is to be determined by a Pensky-Martens Closed Cup Tester, using the test method specified in American Society of Testing and Materials (ASTM) Standard D-93-79 or D-93-80, or a Setaflash Closed Cup Tester, using the test method specified in ASTM Standard D-3278-78, or as determined by an equivalent test method approved by the Administrator under procedures set forth in 40 CFR 260.20 and 260.21 (see “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,” 3rd Ed., as amended, EPA, OSWER, SW-846, Methods 1010 and 1020<sup>12</sup>). (Non-liquid

<sup>10</sup> Note that characteristic only wastes (which are neither wastewater mixtures or RCRA listed hazardous wastes when generated) may be treated so that they no longer exhibit any of the four characteristics of a hazardous waste. However, these wastes may still be subject to the requirements of 40 CFR Part 268, even if they no longer exhibit a hazardous characteristic at the point of land disposal. After treatment this waste must not exhibit any RCRA hazardous waste characteristic and must meet applicable treatment standards before it can be considered a non-hazardous waste (see 57 FR 37263, August 18, 1992, and 58 FR 29869, May 24, 1993).

<sup>11</sup> Note that hazardous and mixed waste samples analyzed for waste characteristics or composition, and samples undergoing treatability studies may be exempt from all or part of the RCRA regulations if they are managed in accordance with 40 CFR 261.4 (d), (e) or (f).

<sup>12</sup> EPA incorporated by reference into the RCRA regulations (58 FR 46040, August 31, 1993), a third edition (and its updates) of “Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods.” The updates can be found in 60 FR 3089, January 13, 1995 (update II), 59 FR 458, January 4, 1994 (update IIA), 60 FR 17001, April 4, 1995

<sup>8</sup> Generators who also treat their waste are subject to the requirements for treatment facilities unless they treat waste in accumulation tanks, containers, or containment buildings, for 90 days or less in accordance with 40 CFR 262.34(a). Treatment facilities must periodically test the treated waste residue from prohibited wastes to determine whether it meets the best demonstrated available technology (BDAT) treatment standards and may not rely on materials and process knowledge to make this determination (40 CFR 268.7(b)). This testing must be conducted according to the frequency specified in the facility's waste analysis plan (refer to Section IV of this guidance for a detailed discussion of treatment, storage, and disposal facility requirements).

<sup>9</sup> This definition of surrogate should not be confused with the definition of surrogate for the purposes of sampling and analysis quality control in Section 1.1.8 of “Evaluating Solid Waste—Volume IA: Laboratory Test Methods Manual Physical/Chemical Methods.”

wastes, compressed gases, and oxidizers may exhibit the characteristic of ignitability as described in 40 CFR 261.21 (a)(2-4.)

**Corrosivity**—For aqueous solutions, the pH is to be determined by a pH meter using either an EPA test method (i.e., SW-846, Method 9040 or an equivalent test method approved by the Administrator under procedures set forth in 40 CFR 260.20 and 260.21.) For liquids, steel corrosion is to be determined by the test method specified in National Association of Corrosion Engineers (NACE) Standard TM-01-69 as standardized in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," 3rd Ed., as amended (EPA, OSWER, SW-846, Method 1110), or an equivalent test method approved by the Administrator under procedures set forth in 40 CFR 260.20 and 260.21.

**Reactivity**—There are no specified test protocols for reactivity. 40 CFR 261.23 defines reactive wastes to include wastes that have any of the following properties: (1) normally unstable and readily undergoes violent change without detonating; (2) reacts violently with water; (3) forms potentially explosive mixtures with water; (4) generates dangerous quantities of toxic fumes, gases, or vapors when mixed with water; (5) in the case of cyanide- or sulfide-bearing wastes, generates dangerous quantities of toxic fumes, gases, or vapors when exposed to acidic or alkaline conditions; (6) explodes when subjected to a strong initiating force or if heated under confinement; (7) explodes at standard temperature and pressure; or (8) fits within the Department of Transportation's forbidden explosives, Class A explosives, or Class B explosives classifications.<sup>13</sup>

EPA has elected to rely on a descriptive definition for these reactivity properties because of inherent deficiencies associated with available methodologies for measuring such a varied class of effects, with the exception of the properties discussed in No. 5, above. The method used, as guidance but not required, to quantify the reactive cyanide and sulfide bearing wastes is provided in Chapter 7 of "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," 3rd Ed., as amended, EPA, OSWER, SW-846.

**Toxicity Characteristic**—The test method that may be used to determine whether a waste exhibits the toxicity characteristic (TC) is the Toxicity Characteristic Leaching Procedure (TCLP), as described in 40 CFR Part 261, Appendix II (SW-846, Method 1311). The TCLP was modified and revised in 55 FR 11798, March 29, 1990. Note that this revised TCLP is used (in most cases) for land disposal restriction compliance determinations as well. Differences between the TCLP and the previously required Extraction Procedure (EP) include improved

analysis of the leaching of organic compounds, the elimination of constant pH adjustment, the addition of a milling or grinding requirement for solids (waste material solids must be milled to particles less than 9.5 mm in size), and other more detailed alterations.<sup>14</sup> Additionally, the TC rule added 25 organic compounds to the toxicity characteristic.

The TCLP (Method 1311) recommends the use of a minimum sample size of 100 grams (solid and liquid phases as described in Section 7.2). *For mixed waste testing, sample sizes of less than 100 grams can be used, if the analyst can demonstrate that the test is still sufficiently sensitive to measure the constituents of interest at the regulatory levels specified in the TCLP and representative of the waste stream being tested.* Other variances to the published testing protocols are permissible (under 40 CFR 260.20-21), but must be approved prior to implementation by EPA. Use of a sample size of less than 100 grams is highly recommended for mixed wastes with concentrations of radionuclides that may present serious radiation exposure hazards.

Additionally, Section 1.2 of the TCLP allows the option of performing a "total constituent analysis" on a hazardous waste or mixed waste sample, instead of the TCLP. Section 1.2 of Method 1311 states:

If a total analysis of the waste demonstrated that the individual analytes are not present in the waste, or that they are present, but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

For homogenous samples, the use of total constituent analysis in this manner eliminates the need to grind or mill solid waste samples. The grinding or milling step in the TCLP has raised ALARA concerns for individuals who test mixed waste. The use of total constituent analysis, instead of the TCLP, may also minimize the generation of secondary mixed or radioactive waste through the use of smaller sample sizes and reduction, or elimination, of high dilution volume leaching procedures.

<sup>14</sup> Note that when using the TCLP, if any liquid fraction of the waste positively determines that hazardous constituents in the waste are above regulatory levels, then it is not necessary to analyze the remaining fractions of the waste. Extraction using the zero headspace extraction vessel (ZHE) is not required, furthermore, if the analysis of an extract obtained using a bottle extractor demonstrates that the concentration of a volatile compound exceeds the specified regulatory levels. The use of a bottle extractor, however, may not be used to demonstrate that the concentration of a volatile compound is below regulatory levels (40 CFR Part 261 Appendix II Sections 1.3 and .4).

### *Flexibility in Mixed Waste Testing*

Flexibility exists in the hazardous waste regulations for generators, TSDFs, and mixed waste permit writers to tailor mixed waste sampling and analysis programs to address radiation hazards. For example, upon the request of a generator, a person preparing a RCRA permit for a TSDF has the flexibility to minimize the frequency of mixed waste testing by specifying a low testing frequency in a facility's waste analysis plan. EPA believes, as stated in 55 FR 22669, June 1, 1990, that "the frequency of testing is best determined on a case-by-case basis by the permit writer."

EPA's hazardous waste regulations also allow a mixed waste facility the latitude to change or replace EPA's test methods (i.e., *Test Methods for Evaluating Solid Waste* (SW-846)) to address radiation exposure concerns. There are only fourteen sections of the hazardous waste regulations that require the use of specific test methods or appropriate methods found in SW-846 which are outlined in Appendix A.<sup>15</sup> However, any person can request EPA for an equivalent testing or analytical method that would replace the required EPA method (see 40 CFR 260.21).

In a recent amendment to the testing requirements, EPA added language to SW-846 that describes fourteen citations in the RCRA program (listed in Appendix A) where the use of SW-846 methods is mandatory (Update II, 60 FR 3089, January 13, 1995). In all other cases, the RCRA program functions under what we call the Performance Based Measurement System (PBMS) approach to monitoring. Language clarifying this approach was included in the final FR Notice which promulgated Update III (62 FR 32542, June 13, 1997) and in appropriate sections (Disclaimer, Preface and Overview, and Chapter 2) of SW-846. Under PBMS, the regulation and/or permit focus is on the question(s) to be answered by the monitoring, the degree of confidence (otherwise known as the Data Quality Objective (DQO)) or the measurement quality objectives (MQO) that must be achieved by the permittee to have demonstrated compliance, and the specific data that must be gathered and documented by the permittee to demonstrate that the objectives were actually achieved. "Any reliable method" may be used to demonstrate that one can see the analytes of concern in the matrix of

<sup>15</sup> With the exception of the fourteen areas (see Appendix D) where test methods are required by hazardous waste regulation, use of EPA's *Test Methods for the Evaluation of Solid Waste* (SW-846) is not required, and should be viewed as guidance on acceptable sampling and analysis methods.

(update IIB), and 62 FR 32452, June 13, 1996 (update IIB). Hazardous and mixed waste generators and management facilities should verify that the analytical method that they use to analyze hazardous waste has not been superseded in the third edition.

<sup>13</sup> When evaluating test protocols for explosive mixed waste, consideration should be given to the likelihood for dispersing radioactivity during detonation. Using process knowledge or a surrogate material would, in most instances, be appropriate for these wastes.

concern at the levels of concern. Additional reference documents on the characterization and testing methods are listed in Appendix C.

NRC regulations do not describe specific testing requirements for wastes to determine if a waste is radioactive. However, both NRC and Department of Transportation regulations contain requirements applicable to characterizing the radioactive content of the waste before shipment. For example, NRC's regulations in 10 CFR 20.2006 require that the waste manifest include, as completely as practicable, the radionuclide identity and quantity, and the total radioactivity. NRC regulations also require that generators determine the disposal Class of the radioactive waste, and outline waste form requirements that must be met before the waste is suitable for land disposal. These regulations are referenced in 10 CFR 20.2006, and are outlined in detail at 10 CFR 61.55 and 61.56. Mixed waste generators are reminded that both RCRA waste testing and NRC waste form requirements must be satisfied. Generators may also be required to amend their NRC or Agreement State licenses in order to perform the tests required under RCRA. In addition, if an NRC licensee uses an outside laboratory to test his or her waste, that laboratory may be required to possess an NRC or Agreement State license. It is the responsibility of the generator to determine if the outside laboratory possesses the proper license(s) prior to transferring the waste to the laboratory for testing.

Where radioactive wastes (or wastes suspected of being radioactive) are involved in testing, it has been suggested that the testing requirements of RCRA may run counter to the aims of the AEA. The AEA requirements that have raised inconsistency concerns with respect to RCRA testing procedures include ALARA, criticality, and security. Neither EPA nor NRC is aware of any specific instances where RCRA compliance has been inconsistent with the AEA. However, both agencies acknowledge the potential for an inconsistency to occur.<sup>16</sup> A licensee or applicant who suspects that an inconsistency may exist should contact both the AEA and RCRA regulatory agencies. These regulatory agencies may deliberate and consult on whether there is an unresolvable inconsistency and, if one exists, they may attempt to fashion

the necessary relief from the particular RCRA provision that gives rise to the inconsistency. However, all other RCRA regulatory requirements would apply. That is, such a conclusion does not relieve hazardous waste facility owner/operators of the responsibility to ensure that the mixed waste is managed in accordance with all other applicable RCRA regulatory requirements. Owner/operators of mixed waste facilities are encouraged to address and document this potential situation and its resolution in the RCRA facility waste analysis plan which must be submitted with the Part B permit application, or addressed in a permit modification.

Both agencies also believe that the potential for inconsistencies can be reduced significantly by a better understanding of the RCRA requirements, a greater reliance on materials and process knowledge, the use of surrogate materials when possible, and the use of controlled atmosphere apparatuses for mixed waste testing. Where testing is conducted, the use of glove boxes and other controlled atmosphere apparatuses during the testing of the radioactive waste material lessens radiation exposure concerns significantly. These protective measures may also help to reconcile the required testing requirements (including milling) with concerns about maintaining exposures to radiation ALARA and complying with other AEA protective standards. If such protective measures do not exist, or do not adequately reduce individual exposure to radiation or address other factors of concern, relief may be available under Section 1006 of RCRA.

#### **V. Determinations by Treatment, Storage, or Disposal Facility Owner/Operators and Certain Generators to Ensure Proper Waste Management**

##### *General Waste Analysis*

Owner/operators of facilities that treat, store, or dispose of hazardous wastes must obtain a chemical and physical analysis of a representative sample of the waste (see 40 CFR 264.13 for permitted facilities, or 40 CFR 265.13 for interim status facilities).<sup>17</sup> The purpose of this analysis is to assure that owner/operators have sufficient information on the properties of the waste to be able to treat, store, or

dispose of the waste in a safe and appropriate manner.

The waste analysis may include data developed by the generator, and existing, published, or documented data on the hazardous waste or on hazardous waste generated from similar processes. In some instances, however, information supplied by the generator may not fully satisfy the waste analysis requirement. For example, in order to treat a particular waste, one may need to know not only the chemical composition of the waste, but also its compatibility with the techniques and chemical reagents used at the treatment facility. Where such information is not otherwise available, the owner/operator will be responsible for gathering relevant data on the waste in order to ensure its proper management.

The analysis must be repeated only if the previous analyses are inaccurate or needs updating. EPA regulations at 40 CFR 264.13(a)(3) do require that, at a minimum, a waste must be re-analyzed if:

(1) The owner/operator is notified, or has reason to believe, that the process or operation generating the waste has changed [in a way such that the hazardous property or characteristics of the waste would change]; and

(2) For off-site facilities, when the results of the verification analysis indicate that the [composition or characteristics of the] waste does not match the accompanying manifest or shipping paper.

The requirements and frequency of waste analysis for a given facility are described in the facility's waste analysis plan. As required by 40 CFR 264.13(b), the waste analysis plan must specify the parameters for which each hazardous waste will be analyzed; the rationale for selecting these parameters (i.e., how analysis for these parameters will provide sufficient information on the waste's properties); and the test methods that will be used to test for these parameters. The waste analysis plan also must specify the sampling method that will be used to obtain a representative sample of the waste to be analyzed; the frequency with which the initial analysis of the waste will be reviewed or repeated, to ensure that the analysis is accurate and up to date; and, for off-site facilities, the waste analyses to be supplied by the hazardous waste generators. Finally, the waste analysis plan must note any additional waste analysis requirements specific to the waste management method employed, such as the analysis of the waste feed to be burned in an incinerator.

The appropriate parameters for each waste analysis plan are determined on an individual basis as part of the permit

<sup>16</sup> An inconsistency occurs when compliance with one statute or set of regulations would necessarily cause non-compliance with the other. It may stem from a variety of considerations, including those related to occupational exposure, criticality, and other safeguards.

<sup>17</sup> A representative sample is defined in 40 CFR 260.10 as "a sample of a universe or whole (e.g., waste pile, lagoon, ground water) which can be expected to exhibit the average properties of the universe or whole." For further guidance see Chapter 9 of the EPA's testing guidance entitled *Test Methods for Evaluating Solid Waste* or SW-846.



application review process. To reduce the inherent hazards of sampling and analyzing radioactive material, and in particular, the potential risk to workers from exposure to radiation posed by duplicative testing of mixed wastes, redundant testing by the generator and off-site facilities should be avoided. In addition, waste analysis plans must include provisions to keep exposures to radiation ALARA, and incorporate relevant AEA-related requirements and regulations.

#### *Analysis Required to Verify Off-site Shipments*

The owner/operator of a facility that receives mixed waste from off-site must inspect and, *if necessary*, analyze each hazardous waste shipment received at the facility to verify that it matches the identity of the waste specified on the accompanying LDR notification or manifest (see 40 CFR 264.13 or 265.13(c)). This testing is known as verification testing. Such inspections and analysis will follow sampling and testing procedures set forth in the facility's waste analysis plan, which is kept at the facility.

It should also be emphasized that, where analysis is necessary, *RCRA regulations do not necessarily require the analysis of every movement of waste received at an off-site facility*. As explained above, the purpose of the waste analysis is to verify that the waste received at off-site facilities is correctly identified, and to provide enough information to ensure that it is properly managed by the facilities.

For example, if a facility receives a shipment of several sealed drums of mixed waste, a representative sample from only one drum may be adequate, if the owner/operator has reason to believe that the chemical composition of the waste is identical in every drum. In such a case, the drum containing the least amount of measurable radioactivity could be sampled to minimize radiation exposures (variations in radioactivity do not necessarily suggest different chemical composition). This procedure also would apply to a shipment of several types of waste. If the owner/operator has reason to believe that the drums in the shipment contain different wastes, then selecting a representative sample might involve drawing a sample from each drum or drawing a sample from one drum in each "set" of drums containing identical wastes. Once this waste analysis requirement has been satisfied, routine retesting of later shipments would not be required if the owner/operator can determine that the properties of the waste he or she manages will not change.

#### *Fingerprint Analysis Versus Full Scale Analysis*

Full scale analysis (i.e., detailed physical and chemical analysis) may be used to comply with the waste analysis plan, including verification of off-site shipments. However, for mixed waste, abbreviated analysis or "fingerprint analysis" may be more appropriate to meet general waste analysis requirements. The test procedure should be determined on a case-by-case basis.

Fingerprint analysis (which may involve monitoring pH, percent water, and cyanide content) is particularly recommended for mixed waste streams with high radiation levels that are received by an off-site TSDF for RCRA waste manifest verification purposes. It may be appropriate to use full scale analysis, instead of, or after, fingerprint analyses, if the facility suspects that the waste was not accurately characterized by the generator, information provided by a generator is incomplete, waste is received for the first time, or the generator changes a process or processes that produced the waste.

#### *Generators Who Treat LDR Prohibited Waste In Tanks, Containers or Containment Buildings To Meet LDR Treatment Requirements*

Hazardous waste generators may treat hazardous wastes in tanks or containers without obtaining a permit if the treatment is done in accordance with the accumulation timeframes and requirements in 40 CFR 262.34. However, generators who treat hazardous waste (including mixed wastes) to meet the EPA treatment standards for land disposal prohibited wastes must also prepare a waste analysis plan similar to that prepared by TSDFs. The plan must be based on a detailed analysis of a representative sample of the LDR prohibited waste that will be treated. In addition, the plan should include all the information that is necessary to treat the waste, including the testing frequency (See 40 CFR 268.7(a)(5)).

#### **VI. Determinations Under the Land Disposal Restrictions**

Generators, as well as treatment facilities and land disposal facilities, that handle mixed waste may have to obtain or amend their radioactive materials licenses if they test or treat mixed waste under the LDRs. The following discussion assumes that generators and treatment and disposal facilities have satisfied the requirement to obtain, or amend, their radioactive materials licenses, as appropriate.

Waste knowledge may also be used to satisfy certain waste characterization

requirements imposed by the LDRs for mixed wastes. The Hazardous and Solid Waste Amendments (HSWA) to RCRA (P.L. 98-616), enacted on November 8, 1984, established the LDR program. This Congressionally mandated program set deadlines (RCRA Sections 3004(d)-(g)) for EPA to evaluate all hazardous wastes and required EPA to set levels, or methods, of treatment which would substantially diminish the toxicity of the waste, or minimize the likelihood of migration of hazardous constituents from any RCRA waste. Beyond specified dates, prohibited wastes that do not meet the treatment standards before they are disposed of, are banned from land disposal unless they are disposed of in a so-called "no-migration" unit (i.e., a unit where the EPA Administrator has granted a petition which successfully demonstrated to a reasonable degree of certainty that there will be no migration of hazardous constituents from the disposal unit for as long as the wastes remain hazardous) (40 CFR 268.6). Certain categories of prohibited wastes also may be granted extensions of the effective dates of the land disposal prohibitions (i.e., case-by-case and national capacity variances (40 CFR 268.5 and Subpart C, respectively). However, these wastes are still restricted and, if disposed in landfills or surface impoundments, must be disposed of in units meeting the minimum technology requirements.<sup>18</sup>

The requirements of the LDR program apply to generators, transporters, and owner/operators of hazardous waste treatment, storage, and disposal facilities. Not all hazardous wastes are subject to 40 CFR Part 268. For instance, certain wastes that are identified or listed after November 8, 1984, such as newly identified mineral processing wastes for which land disposal prohibitions or treatment standards have not yet been promulgated, are not regulated under 40 CFR Part 268.<sup>19</sup>

<sup>18</sup> A prohibited waste may not be land disposed unless it meets the treatment standards established by EPA. These standards are usually based on the performance of the BDAT. A waste that is subject to an extension, such as a national capacity variance, does not need to comply with the BDAT treatment standards, but is "restricted" and if it is going to be disposed in a landfill or surface impoundment, it can only be disposed of in a unit that meets the minimum technology requirements (MTRs). An exception exists for interim status surface impoundments which may continue receiving newly identified and restricted wastes for four years from the date of promulgation of the listings or characteristics before being retrofitted to meet the MTRs (RCRA Section 3005(j)(6)), so long as the only hazardous wastes in the impoundment are newly identified or listed.

<sup>19</sup> The treatment standards for mineral processing wastes and certain additional newly listed waste streams were proposed in 61 FR 2338, January 25,

### *Determinations by Generators*

Under 40 CFR 268.7(a), generators must determine whether their waste is restricted from land disposal (or determine if they are subject to an exemption or variance from land disposal (40 CFR 268.1)) by testing their waste (or a leachate of the waste developed using the TCLP or, in certain cases, the Extraction Procedure Toxicity Test (EP), or by using waste or process knowledge). If the waste exhibits the characteristic of ignitability (and is not in the High Total Organic Constituents (TOC) Ignitable Liquids Subcategory or is not treated by the "CMBST" or "RORGS" treatment technology in 40 CFR 268.42, Table 1), corrosivity, reactivity and/or organic toxicity, the generator must also determine the underlying hazardous constituents (UHCs) in the waste. Two exceptions to this requirement are: (1) if these wastes are treated in wastewater treatment systems subject to the Clean Water Act (CWA) or CWA equivalent; or, (2) if they are injected into a Class I, non-hazardous Underground Injection Control well. A UHC is any constituent listed in 40 CFR 268.48, Table UTS-Universal Treatment Standards, with the exceptions of nickel, zinc and vanadium, which can reasonably be expected to be present at the point of generation of the hazardous waste, at a concentration above the constituent-specific UTS treatment standard. Determining the presence of the UHCs may be made based on testing or knowledge of the waste. The UHCs must meet the UTS before the waste may be land disposed.

If a generator chooses to test the waste rather than use waste or process knowledge for hazardous waste that is not listed and exhibits a characteristic only, the generator must use the TCLP. The only exception is TC metals.

Until the "Phase IV" LDR rule is promulgated in the spring of 1998, generators who characterize their wastes as TC toxic only for metals may use the EP instead of the TCLP result to determine if their waste is land disposal restricted, because the TC wastes do not have final EPA treatment standards whereas, at this time, the EP metals do. If the EP result is negative, the waste will still be considered hazardous, but is not prohibited from land disposal. The TCLP generally yields similar results as the EP. However, in certain matrices the TCLP yields higher lead and arsenic concentrations than the EP. The rationale for using the EP instead of the TCLP for characteristic wastes is

explained in 55 FR 3865, January 31, 1991. For further guidance on using the EP for the land disposal restriction determination, refer to the Figures 1 and 2, of this guidance.

If a waste is found to be land disposal restricted, generators must determine if the waste can be land disposed without further treatment. A prohibited waste may be land disposed if it meets applicable treatment standards (whether through treatment or simply as generated), or is subject to a variance from the applicable standards. As explained above, this determination can be made either based on knowledge of the waste or by testing the waste, or waste leachate using the TCLP.

Generators who determine that their listed waste meets the applicable treatment standards must certify to this determination and notify the treatment, storage, or land disposal facility that receives the waste (40 CFR 268.7(a)(3)). Notification to the receiving facility must be made with the initial shipment of waste and must include the following information:

- EPA Hazardous Waste Number;
- Certification that the waste delivered to a disposal facility meets the treatment standard, and that the information included in the notice is true, accurate, and complete;
- Waste constituents that will be monitored for compliance if monitoring will not include all regulated constituents, for wastes F001-F005, F039, D001, D002, and D012-D043;
- Whether the waste is a non-wastewater or wastewater;
- The subcategory of the waste (e.g., "D003 reactive cyanide"), if applicable;
- Manifest number; and,
- Waste analysis data (if available).

If a generator determines that a waste that previously exhibited a characteristic is no longer hazardous, or is subject to an exclusion from the definition of hazardous waste, a one-time notification and certification must be placed in the generator's files (40 CFR 268.7(a)(7) or 268.9).

Generators who determine that their waste does not meet the applicable treatment standards must ensure that this waste meets the applicable standards prior to disposal. These generators may treat (or store) their prohibited wastes on-site for 90 days or less in qualified tanks, containers (40 CFR 262.34), or containment buildings (40 CFR 268.50), and/or send their wastes off-site for treatment.<sup>20</sup> When

<sup>20</sup> Non-wastewater residues (e.g., slag) that result from high temperature metals recovery that are excluded from the definition of hazardous waste by meeting the conditions of 40 CFR 261.3(c)(2)(ii)(C),

prohibited listed wastes are sent off-site, generators must notify the treatment facility of the appropriate treatment standards (40 CFR 268.7(a)(2)). This notification must be made with the initial shipment of waste and must include the following information:

- EPA Hazardous Waste Number;
- Waste constituents that the treater will monitor if monitoring will not include all regulated constituents, for wastes F001-F005, F039, D001, D002, and D012-D043;
- Whether the waste is a non-wastewater or wastewater;
- The subcategory of the waste (e.g., "D003 reactive cyanide"), if applicable;
- Manifest number; and,
- Specified information for hazardous debris.

Generators whose wastes are subject to an exemption such as a case-by-case extension under 40 CFR 268.5, an exemption under 40 CFR 268.6 (a no-migration variance), or a nationwide capacity variance under 40 CFR 268, Subpart C must also notify the land disposal facility of the exemption. In addition, records of all notices, certifications, demonstrations, waste analysis data, process knowledge determinations, and other documentation produced pursuant to 40 CFR Part 268 must be maintained by the generator for at least three years from the date when the initial waste shipment was sent to on-site or off-site treatment, storage, or disposal (40 CFR 268.7(a)(8)).

### *Determinations by Treaters and Disposers*

Owner/operators of treatment facilities that receive wastes that do not meet the treatment standards are responsible for treating the wastes to the applicable treatment standards or by the specified technology(ies). In addition, the owner/operators of treatment facilities must determine whether the wastes meet the applicable treatment standards or prohibition levels by testing:

(1) The treatment residues, or an extract of such residues using the TCLP, for wastes with treatment standards expressed as concentrations in the waste extract (40 CFR 268.40); and,

(2) The treated residues (not an extract of the treated residues) for wastes with

and hazardous debris that is excluded from the definition of hazardous waste in 40 CFR 261.3(f) have reduced LDR notification requirements. Specifically, these wastes, and characteristic hazardous wastes that are rendered non-hazardous, do not require a notification and certification accompanying each shipment. Instead, they may be sent to an AEA-licensed facility with a one-time notification and certification sent to the EPA Region or authorized State.

1996, and a second supplemental proposed rule signed April 18, 1997.



treatment standards expressed as concentrations in the waste extract (40 CFR 268.40).

This testing should be done at the frequency established in the facility's waste analysis plan. Owner/operators of treatment facilities, however, do not need to test the treated residues or an extract of the residues if the treatment standard is a specified-technology (i.e., a technology specified in 40 CFR 268.40 or 268.45, Table 1.—Alternative Treatment Standards for Hazardous Debris).

Owner/operators of land disposal facilities under the LDRs are responsible for ensuring that only waste meeting the treatment standards (i.e., wastes not prohibited from disposal or wastes that are subject to an exemption or variance) is land disposed. Like a treatment facility, a disposal facility must test a treatment residue or an extract of the treatment residue, except where the treatment standard is a specified technology.

Owner/operators must periodically test wastes received at the facility for disposal (i.e., independent corroborative testing) as specified in the waste analysis plan to ensure the treatment has been successful and the waste meets EPA treatment standards, except where the treatment standard is expressed as a technology.<sup>21</sup> The results of any waste analyses are placed in a TSDF's operating records along with a copy of all certifications and notices (40 CFR 264.73 or 40 CFR 265.73).<sup>22</sup>

#### *Mixed Waste Under the LDRs*

As clarified in the Land Disposal Restrictions rule published on June 1,

<sup>21</sup> Note that verification testing is a means to verify that the wastes received match the waste description on the manifest, which is required under 40 CFR 264.13 and 40 CFR 265.13(c). The main objective of corroborative testing is to provide an independent verification that a waste meets the LDR treatment standard.

<sup>22</sup> Land disposal facilities must maintain a copy of all LDR notices and certifications transmitted from generators and treaters (40 CFR 268.7(c)).

1990 (see EPA's "Third Third rule," 55 FR 22669, June 1, 1990), the frequency of testing, such as corroborative testing for treatment and disposal facilities, should be determined on a case-by-case basis and specified in the RCRA permit. This flexibility is necessary because of the variability of waste types that may be encountered. Mixed waste is unique for its radioactive/hazardous composition and dual management requirements. Each sampling or analytical event involving mixed waste may result in an incremental exposure to radiation, and EPA's responsibility to protect human health and the environment must show due regard for minimizing this unique risk. These are factors which should be considered in implementing the flexible approach to determining testing frequency spelled out in the Third Third Rule language. This flexible approach encourages reduction in testing where there is little or no variation in the process that generates the waste, or in the treatment process that treats the waste, and an initial analysis of the waste is available. Also, the approach may apply to mixed wastes shipped to off-site facilities, where redundant testing is minimized by placing greater reliance on the characterization developed and certified by earlier generators and treatment facilities. On the other hand, where waste composition is not well-known, testing frequency may be increased. Waste analysis plan conditions in the permits of mixed waste facilities should reflect these principles.

#### *Revised Treatment Standards for Solvent Wastes*

EPA promulgated revised treatment standards for wastewater and non-wastewater spent solvent wastes (F001–F005) in 57 FR 37194, August 18, 1992. The revision essentially converts the treatment standards for the organic spent solvent waste constituents (F001–F005) from TCLP based to total waste constituent concentration based. This

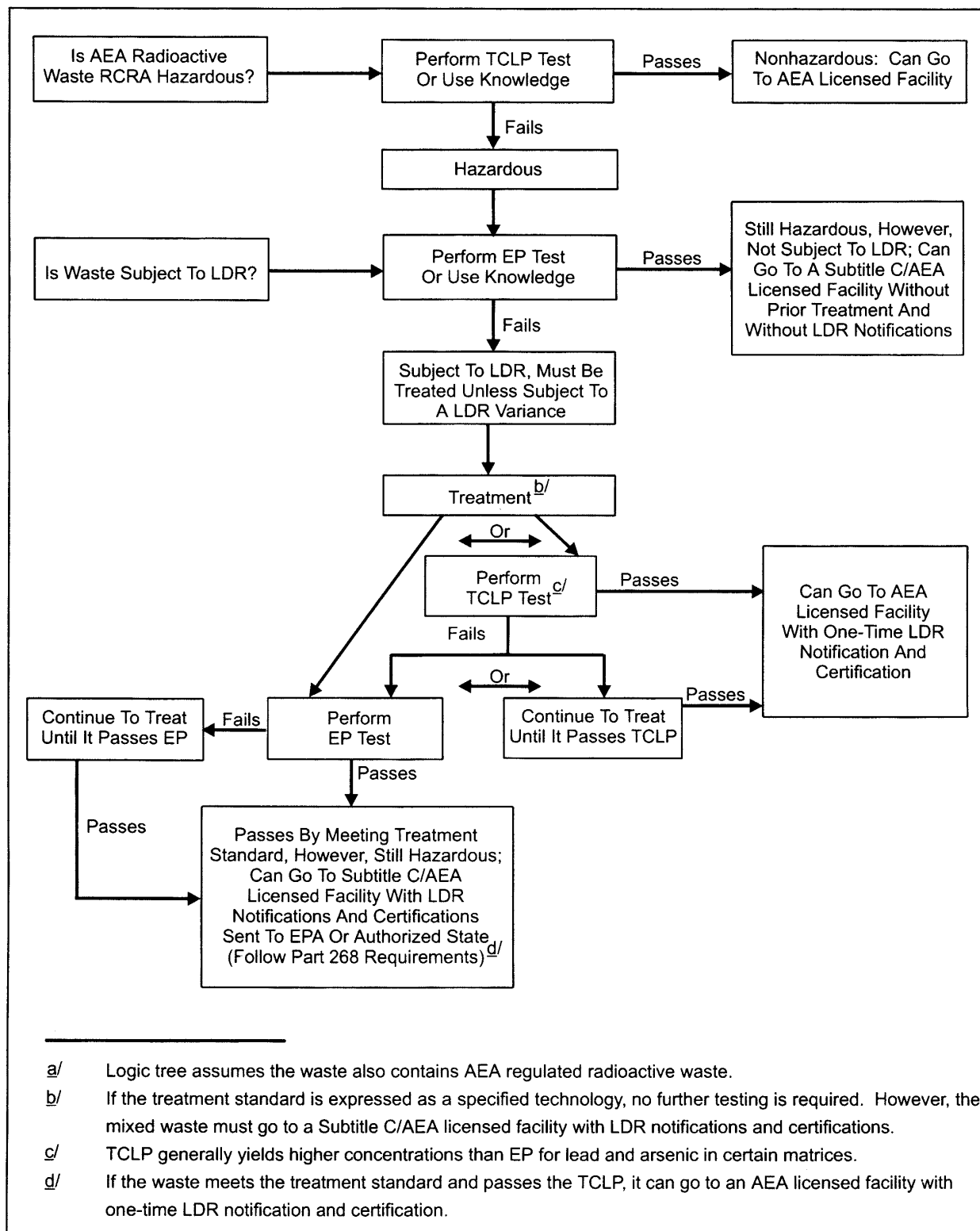
conversion of the spent solvent treatment standards is particularly advantageous to mixed waste generators, since the entire waste stream or treatment residual must be analyzed (instead of a waste or treatment residual extract). This holds true for other mixed waste streams where the hazardous component is measured using a total waste analysis. As discussed in Section IV of this guidance, total constituent analysis has several advantages over the use of the TCLP for high activity waste streams.

EPA and NRC are aware of potential hazards attributable to testing hazardous waste. Moreover, EPA and NRC recognize that the radioactive component of mixed waste may pose additional hazards to laboratory personnel, inspectors, and others who may be exposed during sampling and analysis. All sampling should be conducted in accordance with procedures that minimize exposure to radiation and ensure personnel safety. Further, testing should be conducted in laboratories licensed by NRC or the appropriate NRC Agreement State authority. EPA and NRC believe that a combination of common sense, modified sampling procedures, and cooperation between State and Federal regulatory agencies will minimize any hazards associated with sampling and testing mixed waste.

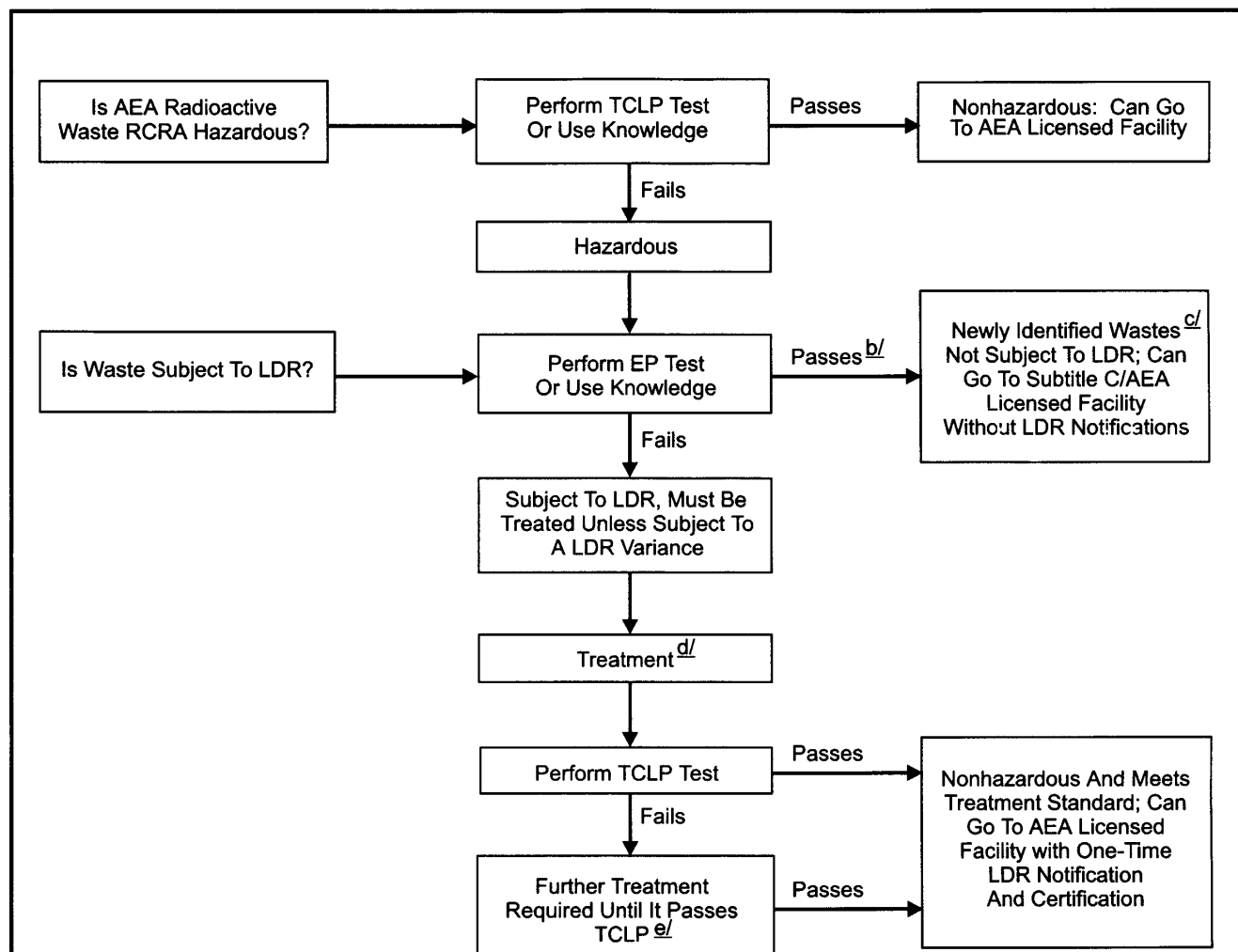
**Note:** Section V, "Determinations under the Land Disposal Restrictions (LDRs)" and the following flow charts represent a brief summary of the Land Disposal Restriction Regulations. They are not meant to be a complete or detailed description of all applicable LDR regulations. For more information concerning the specific requirements, consult the **Federal Registers** cited in the document and the Code of Federal Regulations, Title 40 Parts 124, and 260 through 271.

BILLING CODE 7590-01-P

**FIGURE ONE: TESTING REQUIREMENTS  
FOR CHARACTERISTIC LEAD AND ARSENIC NONWASTEWATERS ONLY<sup>a/</sup>**



**FIGURE TWO: TESTING REQUIREMENTS  
FOR ALL OTHER CHARACTERISTIC METALS<sup>a/</sup>**



<sup>a/</sup> Logic tree assumes the waste also contains AEA regulated radioactive waste.

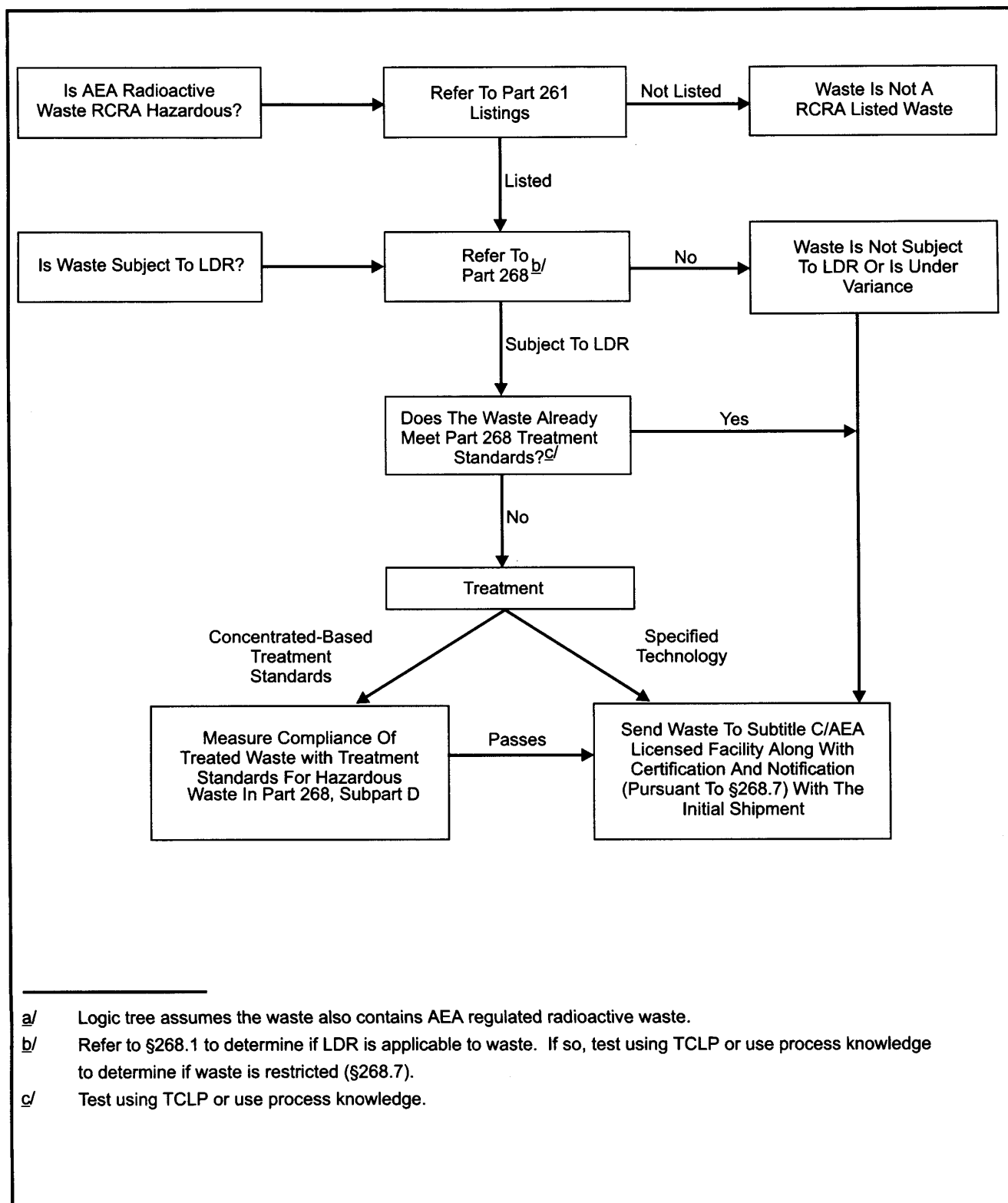
<sup>b/</sup> This should be rare, since the two tests usually yield similar results.

<sup>c/</sup> Wastes exhibiting the toxicity characteristic but not the EP are newly identified wastes and, therefore, are not subject to the land disposal restrictions at this time.

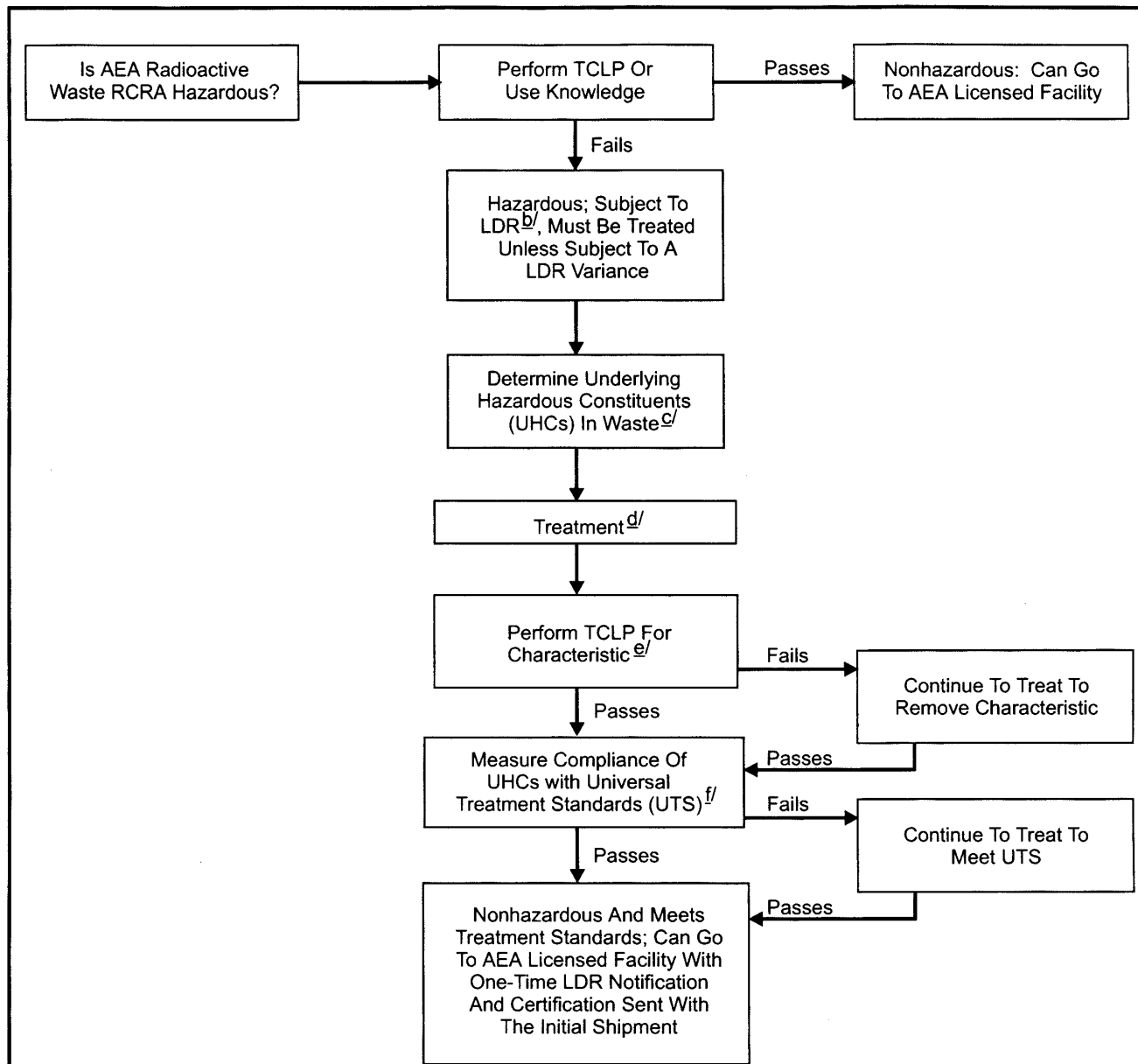
<sup>d/</sup> If the treatment standard is expressed as a specified technology, no further testing is required. However, the mixed waste must go to a Subtitle C/AEA licensed facility with LDR notifications and certifications.

<sup>e/</sup> Selenium is the one exception because it has a treatment standard slightly above the characteristic level.

**FIGURE THREE: TESTING REQUIREMENTS  
FOR RCRA LISTED HAZARDOUS WASTES ONLY<sup>a/</sup>**



**FIGURE FOUR: ORGANIC TOXICITY CHARACTERISTIC (TC)  
WASTES AND PESTICIDE WASTES<sup>a/</sup>**



<sup>a/</sup> Logic tree assumes the waste also contains AEA regulated radioactive waste.

<sup>b/</sup> Restriction applies to TC organic and pesticide wastes managed in non-CWA/non-CWA equivalent/non-Class I SDWA systems only.

<sup>c/</sup> Testing or knowledge of waste may be used. A UHC is any constituent listed in §268.48 Table UTS, except zinc, that can reasonably be expected to be present at the point of generation of the hazardous waste, at a concentration above the constituent-specific UTS treatment standard.

<sup>d/</sup> If the treatment standard is expressed as a specified technology, no further testing is required. However, the mixed waste must go to a Subtitle C/AEA facility with LDR notifications and certifications.

<sup>e/</sup> Refer to the table "Treatment Standards for Hazardous Wastes" in 40 CFR Part 268, Subpart D.

<sup>f/</sup> Compliance should be measured based on the appropriate testing protocols (see SW-846).

**Appendix A—RCRA Regulations That Require Specific EPA Test Methods**

The use of an SW-846 method is mandatory for the following nine Resource Conservation and Recovery Act (RCRA) applications contained in 40 CFR Parts 260 through 270:

- Section 260.22(d)(1)(I)—Submission of data in support of petitions to exclude a waste produced at a particular facility (i.e., delisting petitions);
- Section 261.22(a)(1) and (2)—Evaluations of waste against the corrosivity characteristic;
- Section 261.24(a)—Leaching procedure for evaluation of waste against the toxicity characteristic;
- Section 261.35(b)(2)(iii)(A)—Evaluation of rinsates from wood preserving cleaning processes;

- Sections 264.190(a), 264.314(c), 265.190(a), and 265.314(d)—Evaluation of waste to determine if free liquid is a component of the waste;
- Sections 264.1034(d)(1)(iii) and 265.1034(d)(1)(iii)—Evaluation of organic emissions from process vents;
- Sections 264.1063(d)(2) and 265.1063(d)(2)—Evaluation of organic emissions from equipment leaks;
- Section 266.106(a)—Evaluation of metals from boilers and furnaces;
- Sections 266.112(b)(1) and (2)(I)—Certain analyses in support of exclusion from the definition of a hazardous waste for a residue which was derived from burning hazardous waste in boilers and industrial furnaces;
- Sections 268.7(a), 268.40(a), (b), and (f), 268.41(a), 268.43(a)—Leaching procedure for

evaluation of waste to determine compliance with land disposal treatment standards;

- Sections § 270.19(c)(1)(iii) and (iv), and 270.62(b)(2)(I)(C) and (D)—Analysis and approximate quantification of the hazardous constituents identified in the waste prior to conducting a trial burn in support of an application for a hazardous waste incineration permit; and
- Sections 270.22(a)(2)(ii)(B) and 270.66(c)(2)(I) and (ii)—Analysis conducted in support of a destruction and removal efficiency (DRE) trial burn waiver for boilers and industrial furnaces burning low risk wastes, and analysis and approximate quantification conducted for a trial burn in support of an application for a permit to burn hazardous waste in a boiler and industrial furnace.

**APPENDIX B.—STATES AND TERRITORIES WITH MIXED WASTE AUTHORIZATION**

[As of June 30, 1997]

State/territory	FR date	Effective date	FR cite
Colorado .....	10/24/86	11/7/86	51 FR 37729.
Tennessee .....	6/12/87	8/11/87	52 FR 22443.
S. Carolina .....	7/15/87	9/13/87	52 FR 26476.
Washington .....	9/22/87	11/23/87	52 FR 35556
Georgia .....	7/28/88	9/26/88	53 FR 28383.
Nebraska .....	10/4/88	12/3/88	53 FR 38950.
Kentucky .....	10/20/88	12/19/88	53 FR 41164.
Utah .....	2/21/89	3/7/89	54 FR 7417.
Minnesota .....	4/24/89	6/23/89	54 FR 16361.
Ohio .....	6/28/89	6/30/89	54 FR 27170.
Guam .....	8/11/89	10/10/89	54 FR 32973.
N. Carolina .....	9/22/89	11/21/89	54 FR 38993.
Michigan .....	11/24/89	12/26/89	54 FR 48608.
Texas .....	3/1/90	3/15/90	55 FR 7318.
New York .....	3/6/90	5/7/90	55 FR 7896.
Idaho .....	3/26/90	4/9/90	55 FR 11015.
Illinois .....	3/1/90	4/30/90	55 FR 7320.
Arkansas .....	3/27/90	5/29/90	55 FR 11192.
Oregon .....	3/30/90	5/29/90	55 FR 11909.
Kansas .....	4/24/90	6/25/90	55 FR 17273.
N. Dakota .....	6/25/90	8/24/90	55 FR 25836.
New Mexico .....	7/11/90	7/25/90	55 FR 28397.
Oklahoma .....	9/26/90	11/27/90	55 FR 39274.
Connecticut .....	12/17/90	12/31/90	55 FR 51707.
Florida .....	12/14/90	2/12/91	55 FR 51416.
Mississippi .....	3/29/91	5/28/91	56 FR 13079.
S. Dakota .....	4/17/91	6/17/91	56 FR 15503.
Indiana .....	7/30/91	9/30/91	56 FR 41959.
Louisiana .....	8/26/91	10/26/91	56 FR 41959.
Wisconsin .....	4/24/92	4/24/92	57 FR 15092.
Nevada .....	4/29/92	6/29/92	57 FR 18083.
California .....	7/23/92	8/1/92	57 FR 32725.
Arizona .....	11/23/92	1/22/93	57 FR 54932.
Missouri .....	1/11/93	3/12/93	58 FR 3497.
Alabama .....	3/17/93	5/17/93	58 FR 14319.
Vermont .....	6/7/93	8/6/93	58 FR 31911.
Montana .....	1/19/94	3/21/94	59 FR 2752.
New Hampshire .....	11/14/94	1/13/95	59 FR 56397.
Wyoming .....	10/04/95	10/18/95	60 FR 51925.
Delaware .....	8/8/96	10/7/96	61 FR 41345.
Total: 39 States and 1 Territory.			

**Appendix C: Testing Reference Documents**

The following references provide information on approved methods for testing hazardous waste samples:

- American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 17th Edition. 1989. Available from the Water Pollution Control Federation, Washington, D.C., #S0037.
- U.S. Environmental Protection Agency, *Design and Development of a Hazardous Waste Reactivity Testing Protocol*. EPA Document No. 600/2-84-057, February 1984.
- U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste*. EPA-600/114-79-020. Washington, D.C., 1983.
- U.S. Environmental Protection Agency, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. SW-846. Third Edition (1986) as amended. Available from the Government Printing Office, by subscription, 955-001-00000-1, or from the National Technical Information Service, PB88-239-223. Washington, D.C., January, 1995.
- U.S. Environmental Protection Agency, *The New Toxicity Characteristic Rule: Information and Tips for Generators*. Office of Solid Waste, 530/SW-90-028, April, 1990.
- U.S. Environmental Protection Agency, ORD, and U.S. Department of Energy, *Characterizing Heterogeneous Wastes: Methods and Recommendations*. EPA/600/R-92/033, February 1992.
- U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. "Joint EPA/NRC Guidance on the Definition and Identification of Commercial Mixed Low-Level Radioactive and Hazardous Waste," Directive No. 9432-00-2, October 4, 1989.

**Appendix D: List of Regulations**

- Environmental Protection Agency General Regulations for Hazardous Waste Management, 40 CFR Part 260.
- Environmental Protection Agency Regulations for Identifying Hazardous Waste, 40 CFR Part 261.
- Environmental Protection Agency Regulations for Hazardous Waste Generators, 40 CFR Part 262.
- Environmental Protection Agency Standards for Owners and Operators of Hazardous Waste Treatment, Storage and Disposal Facilities, 40 CFR Part 264.
- Environmental Protection Agency Interim Status Standards for Owners and Operators of Hazardous Waste Facilities, 40 CFR Part 265.
- Environmental Protection Agency Regulations on Land Disposal Restrictions, 40 CFR Part 268.
- Nuclear Regulatory Commission Regulations—Standards for Protection Against Radiation, 10 CFR Part 20.
- Nuclear Regulatory Commission Regulations—Rules of General Applicability to Domestic Licensing of Byproduct Material, 10 CFR Part 30.

Nuclear Regulatory Commission Regulations—Domestic Licensing of Source Material, 10 CFR Part 40.

Nuclear Regulatory Commission Regulations—Domestic Licensing of Production and Utilization Facilities, 10 CFR Part 50.

Nuclear Regulatory Commission Regulations—Licensing Requirements for Land Disposal of Radioactive Waste, 10 CFR Part 61.

Nuclear Regulatory Commission Regulations—Domestic Licensing of Special Nuclear Material, 10 CFR Part 70.

[FR Doc. 97-30528 Filed 11-19-97; 8:45 am]

BILLING CODE 7590-01-P

---

**PRESIDENT'S COMMISSION ON CRITICAL INFRASTRUCTURE PROTECTION TRANSITION OFFICE**


---

**Advisory Committee for the President's Commission on Critical Infrastructure Protection; Meeting**

*Time & Date:* 9:00 a.m.–6:00 p.m., Wednesday, December 3, 1997.

*Action:* Notice of Meeting.

*Summary:* Pursuant to the provisions of the Federal Advisory Committee Act (Pub.L. 92-463, 86 Stat. 770), notice is hereby given for the second meeting of the Advisory Committee on the President's Commission on Critical Infrastructure Protection.

*Address:* The Madison Hotel, 15th and M St., NW, Washington, D.C. 20005. Public seating is limited and is available on a first-come, first-served basis. This facility is accessible to persons with disabilities.

*For Further Information Contact:* Carla Sims, Public Affairs Officer, (703) 696-9395, comments@pccip.gov. Hearing-impaired individuals are advised to contact the Virginia Relay Center (Text Telephone (800) 828-1120 or Voice (800) 828-1140), or their local relay system.

*Supplementary Information:* The Advisory Committee was established by the President to provide expert advice to the Commission as it developed a comprehensive national policy and implementation strategy for protecting the nation's critical infrastructures. The Committee is co-chaired by the Honorable Jamie Gorelick, Vice Chair of Fannie Mae, and the Honorable Sam Nunn, Partner with the law firm of King & Spaulding. The Committee currently consists of 14 members representing various industry sectors.

*Purpose of the Meeting:* This is the second advisory meeting of the Committee. The Committee will review and discuss the recommendations contained in the Commission's report to the President, "Critical Foundations: Protecting America's Infrastructure's."

*Tentative Agenda:* The Advisory Committee meeting will review and discuss

the recommendations contained in the Commission's report. The unclassified report is available electronically from the Commission's site on the World Wide Web (<http://www.pccip.gov/>).

*Public Participation:* The morning session of the meeting will be open to the public. Written comments may be filed with the Commission after the meeting. Written comments may be given to the Designated Federal Officer after the conclusion of the open meeting; mailed to the Commission at P.O. Box 46258, Washington, D.C. 20050-6258; or emailed to comments@pccip.gov/.

*Closed Meeting Deliberations:* In accordance with Section 10(d) of the Federal Advisory Committee Act, Pub. L. 92-463 [5 U.S.C. App II, (1982)], it has been determined that the afternoon session concerns matters listed in 5 U.S.C. 552b (c)(1)(1982). Therefore, the afternoon meeting will be closed to the public in order for the committee to discuss classified material.

**Robert E. Giovagnoni,**

*General Counsel, President's Commission on Critical Infrastructure Protection Transition Office.*

[FR Doc. 97-30501 Filed 11-19-97; 8:45 am]

BILLING CODE 3110--\$-P

---

**OFFICE OF THE UNITED STATES TRADE REPRESENTATIVE**


---

**Notice of Meeting of the Advisory Committee for Trade Policy and Negotiations**

**AGENCY:** Office of the United States Trade Representative.

**ACTION:** Notice that the December 4, 1997, meeting of the Advisory Committee for Trade Policy and Negotiations will be held from 10:00 a.m. to 2:00 p.m. The meeting will be closed to the public from 10:00 a.m. to 1:30 p.m. and open to the public from 1:30 p.m. to 2:00 p.m.

**SUMMARY:** The Advisory Committee for Trade Policy and Negotiation will hold a meeting on December 4, 1997 from 10:00 a.m. to 2:00 p.m. The meeting will be closed to the public from 10:00 a.m. to 1:30 p.m. The meeting will include a review and discussion of current issues which influence U.S. trade policy. Pursuant to Section 2155(f)(2) of Title 19 of the United States Code, I have determined that this meeting will be concerned with matters the disclosure of which would seriously compromise the development by the United States Government of trade policy, priorities, negotiating objectives or bargaining positions with respect to the operation of any trade agreement and other matters arising in connection with the development, implementation and administration of the trade policy of the United States. The meeting will be open

### § 835.3

#### WEIGHTING FACTORS FOR VARIOUS ORGANS AND TISSUES—Continued

Organs or tissues, T	Weighting factor, $w_T$
Bone surfaces .....	0.03
Remainder <sup>1</sup> .....	0.30
Whole body <sup>2</sup> .....	1.00

<sup>1</sup>“Remainder” means the five other organs or tissues, excluding the skin and lens of the eye, with the highest dose (e.g., liver, kidney, spleen, thymus, adrenal, pancreas, stomach, small intestine, and upper large intestine). The weighting factor for each remaining organ or tissue is 0.06.

<sup>2</sup>For the case of uniform external irradiation of the whole body, a weighting factor ( $w_T$ ) equal to 1 may be used in determination of the effective dose equivalent.

*Whole body* means, for the purposes of external exposure, head, trunk (including male gonads), arms above and including the elbow, or legs above and including the knee.

(c) Terms defined in the Atomic Energy Act and not defined in this part are used consistent with the meanings given in the Act.

[58 FR 65485, Dec. 14, 1993, as amended at 63 FR 59680, Nov. 4, 1998]

#### § 835.3 General rule.

(a) No person or DOE personnel shall take or cause to be taken any action inconsistent with the requirements of:

(1) This part; or

(2) Any program, plan, schedule, or other process established by this part.

(b) With respect to a particular DOE activity, contractor management shall be responsible for compliance with the requirements of this part.

(c) Where there is no contractor for a DOE activity, DOE shall ensure implementation of and compliance with the requirements of this part.

(d) Nothing in this part shall be construed as limiting actions that may be necessary to protect health and safety.

(e) For those activities that are required by §§ 835.102, 835.901(e), 835.1202(a), and 835.1202(b), the time interval to conduct these activities may be extended by a period not to exceed 30 days to accommodate scheduling needs.

[58 FR 65485, Dec. 14, 1993, as amended at 63 FR 59682, Nov. 4, 1998]

#### § 835.4 Radiological units.

Unless otherwise specified, the quantities used in the records required by this part shall be clearly indicated in special units of curie, rad, roentgen, or

### 10 CFR Ch. III (1–1–01 Edition)

rem, including multiples and subdivisions of these units. The SI units, becquerel (Bq), gray (Gy), and sievert (Sv), are only provided parenthetically in this part for reference with scientific standards.

[58 FR 65485, Dec. 14, 1993, as amended at 63 FR 59682, Nov. 4, 1998]

#### Subpart B—Management and Administrative Requirements

#### § 835.101 Radiation protection programs.

(a) A DOE activity shall be conducted in compliance with a documented radiation protection program (RPP) as approved by the DOE.

(b) The DOE may direct or make modifications to a RPP.

(c) The content of each RPP shall be commensurate with the nature of the activities performed and shall include formal plans and measures for applying the as low as reasonably achievable (ALARA) process to occupational exposure.

(d) The RPP shall specify the existing and/or anticipated operational tasks that are intended to be within the scope of the RPP. Except as provided in § 835.101(h), any task outside the scope of a RPP shall not be initiated until an update of the RPP is approved by DOE.

(e) The content of the RPP shall address, but shall not necessarily be limited to, each requirement in this part.

(f) The RPP shall include plans, schedules, and other measures for achieving compliance with regulations of this part. Unless otherwise specified in this part, compliance with amendments to this part shall be achieved no later than 180 days following approval of the revised RPP by DOE. Compliance with the requirements of § 835.402(d) for radiobioassay program accreditation shall be achieved no later than January 1, 2002.

(g) An update of the RPP shall be submitted to DOE:

(1) Whenever a change or an addition to the RPP is made;

(2) Prior to the initiation of a task not within the scope of the RPP; or

(3) Within 180 days of the effective date of any modifications to this part.



## Department of Energy

## § 835.203

(h) Changes, additions, or updates to the RPP may become effective without prior Department approval only if the changes do not decrease the effectiveness of the RPP and the RPP, as changed, continues to meet the requirements of this part. Proposed changes that decrease the effectiveness of the RPP shall not be implemented without submittal to and approval by the Department.

(i) An initial RPP or an update shall be considered approved 180 days after its submission unless rejected by DOE at an earlier date.

[58 FR 65485, Dec. 14, 1993, as amended at 63 FR 59682, Nov. 4, 1998]

### § 835.102 Internal audits.

Internal audits of the radiation protection program, including examination of program content and implementation, shall be conducted through a process that ensures that all functional elements are reviewed no less frequently than every 36 months.

[63 FR 59682, Nov. 4, 1998]

### § 835.103 Education, training and skills.

Individuals responsible for developing and implementing measures necessary for ensuring compliance with the requirements of this part shall have the appropriate education, training, and skills to discharge these responsibilities.

[63 FR 59682, Nov. 4, 1998]

### § 835.104 Written procedures.

Written procedures shall be developed and implemented as necessary to ensure compliance with this part, commensurate with the radiological hazards created by the activity and consistent with the education, training, and skills of the individuals exposed to those hazards.

[63 FR 59682, Nov. 4, 1998]

## Subpart C—Standards for Internal and External Exposure

### § 835.201 [Reserved]

### § 835.202 Occupational dose limits for general employees.

(a) Except for planned special exposures conducted consistent with § 835.204 and emergency exposures authorized in accordance with § 835.1302, the occupational dose received by general employees shall be controlled such that the following limits are not exceeded in a year:

(1) A total effective dose equivalent of 5 rems (0.05 sievert);

(2) The sum of the deep dose equivalent for external exposures and the committed dose equivalent to any organ or tissue other than the lens of the eye of 50 rems (0.5 sievert);

(3) A lens of the eye dose equivalent of 15 rems (0.15 sievert); and

(4) A shallow dose equivalent of 50 rems (0.5 sievert) to the skin or to any extremity.

(b) All occupational doses received during the current year, except doses resulting from planned special exposures conducted in compliance with § 835.204 and emergency exposures authorized in accordance with § 835.1302, shall be included when demonstrating compliance with §§ 835.202(a) and 835.207.

(c) Doses from background, therapeutic and diagnostic medical radiation, and participation as a subject in medical research programs shall not be included in dose records or in the assessment of compliance with the occupational dose limits.

[58 FR 65485, Dec. 14, 1993, as amended at 63 FR 59682, Nov. 4, 1998]

### § 835.203 Combining internal and external dose equivalents.

(a) The total effective dose equivalent during a year shall be determined by summing the effective dose equivalent from external exposures and the

## **§§ 835.902–835.903**

(a) or (b) of this section, the escort shall:

(1) Have completed radiation safety training, examinations, and performance demonstrations required for entry to the area and performance of the work; and

(2) Ensure that all escorted individuals comply with the documented radiation protection program.

(e) Radiation safety training shall be provided to individuals when there is a significant change to radiation protection policies and procedures that may affect the individual and at intervals not to exceed 24 months. Such training provided for individuals subject to the requirements of § 835.901(b)(1) and (b)(2) shall include successful completion of an examination.

[63 FR 59685, Nov. 4, 1998]

## **§§ 835.902–835.903 [Reserved]**

### **Subpart K—Design and Control**

#### **§ 835.1001 Design and control.**

(a) Measures shall be taken to maintain radiation exposure in controlled areas ALARA through physical design features and administrative control. The primary methods used shall be physical design features (e.g., confinement, ventilation, remote handling, and shielding). Administrative controls shall be employed only as supplemental methods to control radiation exposure.

(b) For specific activities where use of physical design features is demonstrated to be impractical, administrative controls shall be used to maintain radiation exposures ALARA.

[63 FR 59686, Nov. 4, 1998]

#### **§ 835.1002 Facility design and modifications.**

During the design of new facilities or modification of existing facilities, the following objectives shall be adopted:

(a) Optimization methods shall be used to assure that occupational exposure is maintained ALARA in developing and justifying facility design and physical controls.

(b) The design objective for controlling personnel exposure from external sources of radiation in areas of contin-

## **10 CFR Ch. III (1–1–01 Edition)**

uous occupational occupancy (2000 hours per year) shall be to maintain exposure levels below an average of 0.5 mrem (5 microsieverts) per hour and as far below this average as is reasonably achievable. The design objectives for exposure rates for potential exposure to a radiological worker where occupancy differs from the above shall be ALARA and shall not exceed 20 percent of the applicable standards in § 835.202.

(c) Regarding the control of airborne radioactive material, the design objective shall be, under normal conditions, to avoid releases to the workplace atmosphere and in any situation, to control the inhalation of such material by workers to levels that are ALARA; confinement and ventilation shall normally be used.

(d) The design or modification of a facility and the selection of materials shall include features that facilitate operations, maintenance, decontamination, and decommissioning.

[58 FR 65485, Dec. 14, 1993, as amended at 63 FR 59686, Nov. 4, 1998]

#### **§ 835.1003 Workplace controls.**

During routine operations, the combination of physical design features and administrative controls shall provide that:

(a) The anticipated occupational dose to general employees shall not exceed the limits established at § 835.202; and

(b) The ALARA process is utilized for personnel exposures to ionizing radiation.

[63 FR 59686, Nov. 4, 1998]

### **Subpart L—Radioactive Contamination Control**

SOURCE: 63 FR 59686, Nov. 4, 1998, unless otherwise noted.

#### **§ 835.1101 Control of material and equipment.**

(a) Except as provided in paragraphs (b) and (c) of this section, material and equipment in contamination areas, high contamination areas, and airborne radioactivity areas shall not be released to a controlled area if:

(1) Removable surface contamination levels on accessible surfaces exceed the

# U.S. Department of Energy

Washington, D.C.

## ORDER

DOE O 435.1

Approved: 7-09-99

Review: 7-09-01

### SUBJECT: RADIOACTIVE WASTE MANAGEMENT

---

1. OBJECTIVE. The objective of this Order is to ensure that all Department of Energy (DOE) radioactive waste is managed in a manner that is protective of worker and public health and safety, and the environment.
2. CANCELLATION. This Order cancels DOE 5820.2A, RADIOACTIVE WASTE MANAGEMENT, dated 9-26-88. Cancellation of that Order does not, by itself, modify or otherwise affect any contractual obligation to comply with the Order. The provisions of this canceled Order which have been incorporated by reference in a contract shall remain in effect until the contract is modified.
3. APPLICABILITY.
  - a. DOE Elements. This Order applies to all DOE elements except as stated in item “d.”
  - b. Radioactive Waste. Except as stated in item “d,” this Order applies to the management of:
    - (1) All high-level waste, transuranic waste, and low-level waste, including the radioactive component of mixed waste, for which DOE is responsible;
    - (2) DOE accelerator-produced radioactive waste; and
    - (3) If managed at DOE low-level waste facilities, byproduct materials as defined by section 11e.(2) of the *Atomic Energy Act of 1954*, as amended, or naturally occurring radioactive materials.
  - c. Contractors. The Contractor Requirements Document, Attachment 1, sets forth requirements to be applied to contractors performing work that involves management of DOE radioactive waste at DOE-owned or leased facilities. Contractor compliance with the Contractor Requirements Document will be required to the extent set forth in a contract.

---

**Distribution:**

All Departmental Elements

---

**Initiated By:**

Office of Environmental Management

- d. Exemptions. This Order does not apply to certain DOE programs, facilities, or activities as described below.
- (1) This Order does not apply to activities conducted under the authority of the Director, Naval Nuclear Propulsion Program, as described in Department of Energy *National Security and Military Applications of Nuclear Energy Authorization Act of 1985*, Public Law 98-525.
  - (2) Requirements in this Order that overlap or duplicate requirements of the Nuclear Regulatory Commission (NRC) related to radiation protection, nuclear safety (including quality assurance), and safeguards and security of nuclear material, do not apply to the design, construction, operation, and decommissioning of Office of Civilian Radioactive Waste Management facilities as defined in DOE O 250.1, *Civilian Radioactive Waste Management Facilities – Exemptions from Departmental Orders*.
  - (3) Requirements in this Order that duplicate or conflict with requirements of NRC or an Agreement State do not apply to facilities and activities licensed by the NRC or an Agreement State.
  - (4) Requirements in this Order that duplicate or conflict with the *Waste Isolation Pilot Plant Land Withdrawal Act of 1992*, as amended, Public Law 102-579, including the U.S. EPA's Possessive Certification of the WIPP pursuant to this Act, do not apply to the operation of the Waste Isolation Pilot Plant or the disposal of waste therein.
  - (5) Unless managed in a low-level waste facility, requirements in this Order do not apply to byproduct material as defined in section 11e.(2) of the *Atomic Energy Act of 1954*, as amended, or naturally occurring radioactive material.
  - (6) This Order does not apply to either spent nuclear fuel or non-waste materials.
  - (7) Upon request or on its own initiative, DOE may grant exemptions from the requirements of this Order in accordance with the process provided by DOE M 251.1-1A, *Directives System Manual*, as applicable.

4. REQUIREMENTS.

- a. DOE radioactive waste management activities shall be systematically planned, documented, executed, and evaluated.
- b. Radioactive waste shall be managed to:

- (1) Protect the public from exposure to radiation from radioactive materials. Requirements for public radiation protection are in DOE 5400.5, *Radiation Protection of the Public and the Environment*.
  - (2) Protect the environment. Requirements for environmental protection are in DOE 5400.1, *General Environmental Protection Program*, and DOE 5400.5, *Radiation Protection of the Public and the Environment*.
  - (3) Protect workers. Requirements for radiation protection of workers are in 10 CFR Part 835, *Occupational Radiation Protection*; requirements for industrial safety are in DOE O 440.1A, *Worker Protection Management for DOE Federal and Contractor Employees*.
  - (4) Comply with applicable Federal, State, and local laws and regulations. These activities shall also comply with applicable Executive Orders and other DOE directives.
- c. All radioactive waste shall be managed in accordance with the requirements in DOE M 435.1-1, *Radioactive Waste Management Manual*.
- d. DOE, within its authority, may impose such requirements, in addition to those established in this Order, as it deems appropriate and necessary to protect the public, workers, and the environment, or to minimize threats to property.
5. RESPONSIBILITIES. All DOE elements as specified in 3.a are responsible for implementing the requirements of this Order. See DOE M 435.1-1, *Radioactive Waste Management Manual*, for specific responsibilities.
6. REFERENCES. DOE M 435.1-1, *Radioactive Waste Management Manual* of 7-09-99 and DOE G 435.1-1, *Implementation Guide for DOE M 435.1-1*.
7. CONTACT. Questions concerning this Order should be addressed to the Office of Waste Management at (202) 586-0370.

BY ORDER OF THE SECRETARY OF ENERGY:



THOMAS T. TAMURA  
Acting Director of  
Management and Administration

## CONTRACTOR REQUIREMENTS DOCUMENT

1. In the performance of this contract, the contractor is required to:
  - A. Systematically plan, document, execute, and evaluate the management of DOE radioactive waste and assist the government in planning, executing and evaluating the management of DOE radioactive waste in accordance with the requirements of DOE O 435.1, *Radioactive Waste Management*.
  - B. Assist the government in managing DOE radioactive waste so as to:
    - (1) Protect the public from exposure to radiation from radioactive materials.
    - (2) Protect the environment.
    - (3) Protect workers including following requirements for radiation protection.
  - C. Assist DOE in meeting its obligations and responsibilities under Executive Order 12856, *Federal Compliance with Right-to-Know Laws and Pollution Prevention Requirements*, and Executive Order 13101, *Greening the Government through Waste Prevention, Recycling, and Federal Acquisition*, and *The Pollution Prevention Act of 1990*.
  - D. Comply with the requirements in DOE M 435.1-1, *Radioactive Waste Management Manual*, unless such activities are specifically exempted by DOE O 435.1, Section 3.d., as described below.
    - (1) Activities conducted under the authority of the Director, Naval Nuclear Propulsion Program, as described in Department of Energy *National Security and Military Applications of Nuclear Energy Authorization Act of 1985*, Public Law 98-525.
    - (2) Requirements that overlap or duplicate requirements of the Nuclear Regulatory Commission (NRC) related to radiation protection, nuclear safety (including quality assurance), and safeguards and security of nuclear material, do not apply to the design, construction, operation, and decommissioning of Office of Civilian Radioactive Waste Management facilities as defined in DOE O 250.1, *Civilian Radioactive Waste Management Facilities – Exemptions from Departmental Orders*.

- (3) Requirements that duplicate or conflict with requirements of NRC or an Agreement State do not apply to facilities and activities licensed by the NRC or an Agreement State.
  - (4) Requirements that duplicate or conflict with the *Waste Isolation Pilot Plant Land Withdrawal Act of 1992*, as amended, Public Law 102-579, do not apply to the operation of the Waste Isolation Pilot Plant or the disposal of waste therein.
  - (5) Unless managed in a low-level waste facility, requirements in DOE O 435.1 do not apply to byproduct material as defined in section 11e.(2) of the *Atomic Energy Act of 1954*, as amended, or naturally occurring radioactive material.
  - (6) Spent nuclear fuel or non-waste materials.
  - (7) Upon request or on its own initiative, DOE may grant exemptions from the requirements of DOE O 435.1 in accordance with the process provided by DOE M 251.1-1A, *Directives System Manual*.
- E. Incorporate these requirements into the contracts of all sub-contractors which are involved in the management of DOE radioactive waste.

**U.S. Department of Energy**  
**Washington, D.C.**

**POLICY**

**DOE P 441.1**

4-26-96

**SUBJECT: DEPARTMENT OF ENERGY RADIOLOGICAL  
HEALTH AND SAFETY POLICY**

---

1. PURPOSE. To establish the Department of Energy's Radiological Health and Safety Policy as a basis for the Department's radiological control programs.
2. SCOPE. The provisions of this directive apply to all departmental elements involved in radiological operations, except the Naval Nuclear Propulsion Program, which is separately covered under Executive Order 12344, Public Law 98-525 (42 U.S. Code 7158, Note).
3. POLICY. It is the policy of the Department of Energy to conduct its radiological operations in a manner that ensures the health and safety of all its employees, contractors, and the general public. In achieving this objective, the Department shall ensure that radiation exposures to its workers and the public and releases of radioactivity to the environment are maintained below regulatory limits and deliberate efforts are taken to further reduce exposures and releases as low as reasonably achievable. The Department is fully committed to implementing a radiological control program of the highest quality that consistently reflects this policy.

In meeting this policy, the Department shall:

- A. **Establish and maintain a system of regulatory policy and guidance reflective of national and international radiation protection standards and recommendations.** The Assistant Secretary for Environment, Safety and Health has responsibility for promulgating and maintaining policies, standards, and guidance related to radiological protection. Departmental radiological protection requirements are, at a minimum, consistent with the presidentially approved "Radiation Protection Guidance to the Federal Agencies for Occupational Exposure," which was developed by the Environmental Protection Agency in accordance with its mandated Federal guidance responsibilities. Departmental requirements often are more stringent and reflect, as appropriate, recommendations and guidance from various national and international standards-setting and scientific organizations, including the International Commission on Radiological Protection, the National Council on Radiation Protection and Measurements, the American National Standards Institute, and others. Departmental requirements related to radiological protection will be set forth, as appropriate, in rules and Department of Energy orders, and guidance documents will be issued on acceptable means to implement these requirements.

---

**DISTRIBUTION:**  
All Departmental Elements

**INITIATED BY:**  
Office of the Secretary



- B. **Ensure personnel responsible for performing radiological work activities are appropriately trained.** Standards shall be established to ensure the technical competency of the Department's workforce, as appropriate, through implementation of radiological training and professional development programs.
- C. **Ensure the technical competence of personnel responsible for implementing and overseeing the radiological control program.** An appropriate level of technical competence gained through education, experience, and job-related technical and professional training is a critical component for achieving the goals of the Department's radiological control policy. Qualification requirements commensurate with this objective shall be established for technical and professional radiological control program positions and shall, at a minimum, be consistent with applicable industry standards and promote professional development and excellence in radiological performance as goals.
- D. **Establish and maintain, at all levels, line management involvement and accountability for departmental radiological performance.** The responsibility for compliance with departmental radiological protection requirements, and for minimizing personnel radiation exposure, starts at the worker level and broadens as it progresses upward through the line organization. The Department's line managers are fully responsible for radiological performance within their programs and the field activities and sites assigned to them, and shall take necessary actions to ensure requirements are implemented and performance is monitored and corrected as necessary.
- E. **Ensure radiological measurements, analyses, worker monitoring results and estimates of public exposures are accurate and appropriately made.** The capability to accurately measure and analyze radioactive materials and workplace conditions, and determine personnel radiation exposure, is fundamental to the safe conduct of radiological operations. Policy, guidance, and quality control programs shall be directed toward ensuring such measurements are appropriate, accurate, and based upon sound technical practices.
- F. **Conduct radiological operations in a manner that controls the spread of radioactive materials and reduces exposure to the workforce and the general public and that utilizes a process that seeks exposure levels as low as reasonably achievable.** Radiological operations and activities shall be preplanned to allow for the effective implementation of dose and contamination reduction and control measures. Operations and activities shall be performed in accordance with departmental conduct of operations requirements and shall include reasonable controls directed toward reducing exposure, preventing the spread of radiological contamination, and minimizing the generation of contaminated wastes and the release of effluents.

- G. **Incorporate dose reduction, contamination reduction, and waste minimization features into the design of new facilities and significant modifications to existing facilities in the earliest planning stages.** Wherever possible, facility design features shall be directed toward controlling contamination at the source, eliminating airborne radioactivity, maintaining personnel exposure and effluent releases below regulatory limits, and utilizing a process that seeks exposure levels and releases as low as reasonably achievable. Radiological design criteria shall reflect appropriate consensus recommendations of national and international standards setting groups.
- H. **Conduct oversight to ensure departmental requirements are being complied with and appropriate radiological work practices are being implemented.**

All departmental elements shall conduct their radiological operations in a manner consistent with the above policies and objectives.



HAZEL R. O'LEARY  
Secretary of Energy

**VE HAZARDS DOCUMENTATION FROM THE ROCKY FLATS ENVIRONMENTAL  
TECHNOLOGY SITE**

## Safety Report

Attached is a typical safety report from RFETS which documents the need for this modification. The modification will allow the generator/storage sites the ability to define specific safety criteria before performing VE.

The report from RFETS indicates that broken glass (sharps) is within the waste and could pose a hazard to the VE operator.

## REAL TIME RADIOGRAPHY WASTE PACKAGE REPORT

<b>IDENTIFICATION:</b>		Drum/Box No.: <u>D 82863</u>	Procedure: <u>4-19-NDT-00569 Rev. 3</u>
Control No.: <u>37-03935</u>		Container Type: <u>Drum</u>	
IDC: <u>440</u>	IDC Correct? <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	TRU/LLW: <u>Tru</u>	
Generator Bldg. # <u>771</u>	RTR Bldg. # <u>569</u>	Date Packaged: <u>2-15-94</u>	
<b>ARCHIVES:</b> Tape #: <u>5T-0125 A+B</u>			
Tape Footage Start: <u>01135</u>		End: <u>01625</u>	
<b>LINER(S):</b> Present: <input checked="" type="checkbox"/> Rigid Liner <input checked="" type="checkbox"/> Poly Liner <input type="checkbox"/> 2 <sup>nd</sup> Poly Liner <input checked="" type="checkbox"/> Fiberboard Liner			
Correct? <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No			
If no, explain: _____			
<b>ARE ANY OF THE FOLLOWING PROHIBITED ITEMS PRESENT? If yes, description, location, etc.</b>			
Liquid : Total Amount: _____ ml	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	_____	
Non-radioactive pyrophoric materials?	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	_____	
Non-toxic hazardous waste?	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	_____	
Wastes incompatible with backfill, seal and panel closures materials, container and packaging materials, shipping container materials, or other wastes?	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	_____	
Explosives or compressive gases (such as unvented aerosol containers)?	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	_____	
PCBs with concentrations $\geq 50$ ppm (such as transformers, capacitors, and ballasts)?	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	_____	
Waste exhibiting the characteristics of ignitability, corrosivity or reactivity (EPA Hazardous Waste Numbers of D001, D002, or D003)?	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	_____	
<b>RTR CONTENT DESCRIPTION/COMMENTS/NONCONFORMANCES:</b>			
<u>Glass — and extra plastic packaging</u>			
<u>Glass bottles, and crushed glass bottles</u>			
<b>TEST BOTTLES:</b> Check off value(s) visible: <input checked="" type="checkbox"/> 10 ml <input checked="" type="checkbox"/> 20 ml <input checked="" type="checkbox"/> 40 ml <input checked="" type="checkbox"/> 80 ml <input type="checkbox"/> None			
<b>RESOLUTION CHECK:</b>			
Test pattern resolution? <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No			
<b>ACCEPT/REJECT:</b> <u>accept</u>		<b>AUDIO/VISUAL CHECK:</b> <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	
<b>OPERATORS:</b>			
Print Name		Signature	
Technician: <u>G. Melick</u>	<u>G. Melick</u>	Empl. No.: <u>505366</u>	Date: <u>9-17-00</u>
<b>SUPERVISOR (signature required for LLW):</b>			
Supervisor: _____		Empl. No.: _____ Date: _____	

WASTE CHARACTERIZATION RTR REPORT				
RTR Data		4. Inventory of Waste Container Contents		
Waste Container Identification Number <u>D 82 86.3</u>		Waste Material Parameter		
Control No.: <u>37-03935</u>		Item Present	% of weight	Wgt.* KG
Container Gross Weight <u>189.2 lbs = 86 KG</u>		Iron-based Metal/Alloys		KG
Container Net Weight <u>114.4 lbs = 52 KG</u>		Aluminum based metals		KG
Examining Site <u>Rocky Flats</u>		Other Metals		KG
TRUCON Code <u>RF118A</u>				KG
IDC: <u>440</u>		Other Inorganic Materials	91	47 KG
Waste Matrix Code <u>5 5122</u>				KG
1. Do you recommend the TRUCON Content Code, Waste Matrix Code, or IDC changed? <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		Cellulosics	5	2.7 KG
If yes, what is the recommended change?				KG
2. Waste package fill percentage: - <u>95</u> %		Rubber		KG
				KG
		Plastics (Waste Materials)	44	1.8 KG
			.5	KG
		Organic Matrix		KG
		Inorganic Matrix		KG
				KG
		Soils		KG
		Steel (packaging materials)		29 KG
		Plastics (Packaging Materials)		5 KG
3. QC replicate? <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No				
If yes, brief description of comparison results and reference to original scan:				
4. Comments: <u>Rigid, Poly, Fiberboard liner</u>				
5. Operator <u>G. Melick</u> <span style="float: right;">Print Name</span>				
6. Independent Observation <u>G. Melick</u> <span style="float: right;">Signature</span>				
7. Independent Technical Review <u>J. F. HARNET</u> <span style="float: right;">Employee No. 505766 Date 7-17-00</span>				

\* Estimated weights will be determined using the RTR derived waste materials inventory, Waste Inventory Tables, and HEPA Filter Values of the appropriate RTR procedure.

10

**Attachment D**  
**INFORMATION SUPPORTING ITEM 3**

**ANALYSES OF THE AFFECTS OF FILTER CHANGE ON CONTAINERS**

**CENTRALIZED CONFIRMATION FACILITY TIME-MOTION-DOSE STUDY**

**PIPE OVERPACK CONTAINER**

**ANALYSES OF THE AFFECTS OF FILTER CHANGE ON CONTAINERS AT THE  
ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE**



## TEST PLAN

TEST PLAN  
EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM  
PIPE OVERPACK COMPONENTS

Summary:

An empty Pipe Overpack Component (POC) will be evacuated and filled with a reference standard (i.e., with the field reference standard) with known concentrations of seven volatile organic compounds (VOCs) (see Table 1) using a gas tight seal connection between a sampling manifold that is equipped with sampling canisters, a reference standard and a vacuum pump. The gas inside the POC will be evacuated and replaced with the reference standard gas. A baseline gas sample will be taken just prior to removal and replacement of the gas tight seal on the POC. A test headspace gas sample will be collected from inside the POC immediately after removal/replacement of the gas tight seal. The samples will be analyzed for headspace gas VOCs. The results from the baseline sample will be compared to the results from the test headspace gas sample and the results from these two samples will be compared with the standard values for the reference standard to determine if there is any significant difference between any of them. The test will be repeated several times to evaluate the effect of increasing the time duration that the POC headspace is exposed to room atmosphere.

Table 1  
Known Concentration of VOCs in Reference Standard

VOC Name	Standard Value (ppmv)
Benzene	12.2
cis-1,2-Dichloroethylene	12.0
1,1-Dichloroethane	12.1
1,2-Dichloroethane	12.1
1,1-Dichloroethene	12.3
Tetrachloroethylene	12.2
1,1,1-Trichloroethane	12.0

Purpose:

Testing will evaluate effects on headspace gas VOC concentrations when collecting samples utilizing the gas tight seal sampling methodology. Using the gas tight seal involves opening the drum to expose the top of the POC itself, removing the POC filter and replacing it with a gas tight seal, and drawing a gas sample from the POC through the gas tight seal into a Summa canister. Using this method, a concern has developed that some of the VOCs in the headspace of the POC could escape while the POC filter is exchanged for the gas tight seal, thereby compromising the sample integrity and representativeness. The purpose of this test plan is to evaluate this concern to determine if there is any significant loss of VOCs in the execution of this sampling methodology.

Hypothesis:

There is no difference between the actual gas concentration of VOCs inside a Pipe Overpack Component (POC) and corresponding concentrations in a headspace sample of this same gas collected using the gas tight seal sampling method (i.e., removing the POC filter/plug and installing a gas tight seal to collect the sample).

Reviewed For C... NI  
By T. Sandelwood  
Date 22 AUG 01 UAM  
CEX-073-79

TEST PLAN  
EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM  
PIPE OVERPACK COMPONENTS

## Procedure:

The following steps outline the general procedure to be followed in the execution of this test plan. All headspace sampling, and sample handling, custody, traceability and analysis procedures will be followed during the execution of this test plan.

1. Obtain an empty POC drum and remove the drum lid and associated packaging to expose the lid of the POC.
2. Remove the filter from the POC filter port and attach a gas tight seal that is connected to a sampling manifold equipped with sampling canisters, a vacuum pump and a field reference standard cylinder.
3. Evacuate the POC using the vacuum pump to a pressure of approximately 100 microns of mercury.
4. Perform a rate of rise leak test on the POC. Evacuation and sealing is considered adequate when the rate of rise is less than 5 microns per second.
5. Record the atmospheric pressure, the final POC evacuation pressure (that also corresponds to the initial rate of rise pressure), the final rate of rise pressure, the time interval between the initial and final rate of rise pressures and the calculated rate of rise.
6. Isolate the vacuum pump from the sampling manifold/POC and then slowly add field reference standard through the manifold into the POC.
7. Pressurize the POC with field reference standard to 10 torr or greater above atmospheric pressure. Record this pressure.
8. Isolate the field reference standard from the sampling manifold/POC.
9. Allow the gas inside the POC and manifold to equilibrate for approximately 15 minutes. Record this equilibration time.
10. Withdraw a baseline gas sample into a clean Summa canister from the combined manifold/POC system and record the system pressure after sample collection. This pressure must be greater than atmospheric pressure.
11. Vent the combined manifold/POC system through the manifold to equalize the pressure inside the POC with atmospheric pressure.
12. The following steps are to be performed as they would be performed when actually headspace sampling a POC in accordance with procedure L-4146, Headspace Gas Sampling of Waste Containers:
  - a. Remove the manifold gas tight seal from the POC. (This step is identical to removing the POC filter when executing procedure L-4146.)
  - b. Connect a different manifold gas tight seal to the POC. (This step is identical to attaching the gas tight seal to the POC when executing procedure L-4146.)
  - c. Record the POC exposure time (i.e., the time the POC was not equipped with a gas tight seal).
  - d. Collect a test headspace gas sample from the POC headspace.
  - e. Record the pressure of the manifold/POC system after sample collection.
13. Without removing or changing the gas tight seal, refill the manifold/POC system with field reference standard to 10 torr or greater above atmospheric pressure. Record this pressure.
14. Repeat steps 8 through 13.
15. Analyze all headspace gas samples per WIPP approved procedures.

The POC exposure time will be actually measured in the initial tests to establish a baseline that estimates the time it takes to remove and replace the POC filter with a gas tight seal under routine headspace gas sampling operations. In addition, tests will also be performed at measured exposure times that exceed this average routine time. The specific tests and associated exposure times are presented in Table 2:

## TEST PLAN EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS

Table 2  
POC Exposure Times to be Evaluated

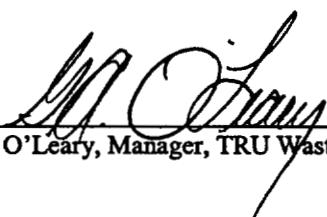
Test Number	POC Exposure Time (minutes)
1	As measured
2	As measured
3	As measured
4	Average as measured time plus 0.5 minutes
5	Average as measured time plus 1 minute
6	Average as measured time plus 2 minutes
7	Average as measured time plus 5 minutes


Use of Results:

Results from each of the baseline samples will be compared with results from the corresponding test POC headspace sample and a relative percent difference (RPD) will be calculated. If the RPD for a pair of samples is less than or equal to 25 % then the two samples satisfy the field quality control sample acceptance criteria for field duplicates. This is interpreted to mean that there is no significant difference, based on the WIPP Hazardous Waste Facility Waste Analysis Plan (WAP), between the two samples. If the samples do not satisfy the RPD criterion, then this will be interpreted to mean that there is a significant difference, based on the WIPP WAP, between the two samples.

Additionally, the results from both the baseline sample and the test POC headspace sample will be compared to the standard values for the field reference standard. If the percent recovery (%R) is between 70 to 130 % for all six analytes, then a sample satisfies the field quality control sample acceptance criteria for field reference standards. This will be interpreted to mean that there is no significant difference, based on the WIPP WAP, between the field reference standard and the sample analyzed. If the %R is not between 70 to 130 % for all six analytes, then a sample does not satisfy the field quality control sample acceptance criteria for field reference standards. This will be interpreted to mean that there is a significant difference, based on the WIPP WAP, between the field reference standard and the sample analyzed.

Concurrence:

  
G. A. O'Leary, Manager, TRU Waste Programs

  
Date

## TEST RESULTS

Summary of Results for the Test Plan for the Evaluation of Gas Tight Seal for Collection of Headspace Gas Samples from Pipe Overpack Components

Results from the execution of the Test Plan for the Evaluation of Gas Tight Seal for Collection of Headspace Gas Samples from Pipe Overpack Components are summarized in Table 1. The results are presented in order of the seven tests that are specified in the Test Plan. For each test, the analysis results for the seven reference standard volatile organic compounds (VOCs) are reported for both the baseline sample and the test sample along with the evaluated exposure time (i.e., the time while the Pipe Overpack Component (POC) vent port was not equipped with a gas tight seal). For each baseline and test sample, the percent recovery (%R) was calculated for each of the seven VOCs and compared to the acceptance criteria for field reference standards given in the WIPP Hazardous Waste Facility Waste Analysis Plan (WAP), Table B1-3. The formula used to calculate the %R is given in Section B3-1 of the WAP (equation B3-5). If the VOC recovery satisfied the acceptance criteria then it is designated as "Pass." If the VOC recovery did not satisfy the acceptance criteria, the VOC is designated as "Fail." Additionally, the results for each of the seven VOCs from the baseline sample were compared with the corresponding results from the test sample by calculating the relative percent difference (RPD) using equation B3-1 presented in Section B3-1 of the WAP. The calculated RPD was then compared to the acceptance criteria for field duplicates specified in the WAP, Table B1-3. Again, if the VOC RPD satisfied the acceptance criteria then it is designated as "Pass" while if it did not satisfy the acceptance criterion it is designated as "Fail."

From the results given in Table 1, no VOC in any of the seven tests failed any of the criteria (%R or RPD). Exposure times ranged from 28 seconds (0.47 minutes) to 329 seconds (5.48 minutes). Therefore, the conclusion of the test is that there is no significant difference, based on the WIPP WAP, between the baseline sample and the corresponding test sample or between the standard values of the reference standard used and either the baseline sample results or the test sample results over the range of exposure times tested. From the results of the subject test plan, sampling of a POC using a gas tight seal does not significantly bias the VOC composition of the headspace gas sample with respect to the VOC composition of the headspace gas itself inside of the POC.

Reviewed For Classification/UCNI  
By 7/2/2004  
Date 22 AUG 01 UAY

CEX-073-95

**Table 1**  
**RESULTS SUMMARY FROM**

**TEST PLAN FOR THE EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS**

**Test 1**

**Exposure Time: 40 seconds (0.67 minutes)**

Baseline Sample ID: 01W7538  
Test Sample ID: 01W7539  
Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	12	98.4	70 to 130 %	Pass	12	98.4	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	14	116.7	70 to 130 %	Pass	13	108	70 to 130 %	Pass	7.4	<=25	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	13	107	70 to 130 %	Pass	7.4	<=25	Pass
1,2-Dichloroethane	12.1	12	99.2	70 to 130 %	Pass	12	99.2	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	12	97.6	70 to 130 %	Pass	8.0	<=25	Pass
Tetrachloroethylene	12.2	12	98.4	70 to 130 %	Pass	11	90.2	70 to 130 %	Pass	8.7	<=25	Pass
1,1,1-Trichloroethane	12	13	108.3	70 to 130 %	Pass	13	108	70 to 130 %	Pass	0.0	<=25	Pass

**Test 2**

**Exposure Time: 31 seconds (0.52 minutes)**

Baseline Sample ID: 01W7540  
Test Sample ID: 01W7541  
Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	12	98.4	70 to 130 %	Pass	12	98.4	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	14	116.7	70 to 130 %	Pass	13	108	70 to 130 %	Pass	7.4	<=25	Pass
1,1-Dichloroethane	12.1	15	124.0	70 to 130 %	Pass	14	116	70 to 130 %	Pass	6.9	<=25	Pass
1,2-Dichloroethane	12.1	13	107.4	70 to 130 %	Pass	12	99.2	70 to 130 %	Pass	8.0	<=25	Pass
1,1-Dichloroethene	12.3	14	113.8	70 to 130 %	Pass	13	106	70 to 130 %	Pass	7.4	<=25	Pass
Tetrachloroethylene	12.2	11	90.2	70 to 130 %	Pass	11	90.2	70 to 130 %	Pass	0.0	<=25	Pass
1,1,1-Trichloroethane	12	13	108.3	70 to 130 %	Pass	13	108	70 to 130 %	Pass	0.0	<=25	Pass

Table 1  
RESULTS SUMMARY FROM

TEST PLAN FOR THE EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS

Test 3

Exposure Time: 28 seconds (0.47 minutes)

Baseline Sample ID: 01W7598

Test Sample ID: 01W7588

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	12	98.4	70 to 130 %	Pass	12	98.4	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	13	108.3	70 to 130 %	Pass	13	108	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	14	116	70 to 130 %	Pass	0.0	<=25	Pass
1,2-Dichloroethane	12.1	12	99.2	70 to 130 %	Pass	12	99.2	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	13	106	70 to 130 %	Pass	0.0	<=25	Pass
Tetrachloroethylene	12.2	11	90.2	70 to 130 %	Pass	11	90.2	70 to 130 %	Pass	0.0	<=25	Pass
1,1,1-Trichloroethane	12	13	108.3	70 to 130 %	Pass	13	108	70 to 130 %	Pass	0.0	<=25	Pass

Test 4

Exposure Time: 62 seconds (1.03 minutes)

Baseline Sample ID: 01W7599

Test Sample ID: 01W7597

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	12	98.4	70 to 130 %	Pass	12	98.4	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	14	116.7	70 to 130 %	Pass	13	108	70 to 130 %	Pass	7.4	<=25	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	14	116	70 to 130 %	Pass	0.0	<=25	Pass
1,2-Dichloroethane	12.1	12	99.2	70 to 130 %	Pass	12	99.2	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	12	97.6	70 to 130 %	Pass	8.0	<=25	Pass
Tetrachloroethylene	12.2	12	98.4	70 to 130 %	Pass	11	90.2	70 to 130 %	Pass	8.7	<=25	Pass
1,1,1-Trichloroethane	12	13	108.3	70 to 130 %	Pass	13	108	70 to 130 %	Pass	0.0	<=25	Pass



**Table 1**  
**RESULTS SUMMARY FROM**

**TEST PLAN FOR THE EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS**

Test 5

Exposure Time: 89 seconds (1.48 minutes)

Baseline Sample ID: 01W7587

Test Sample ID: 01W7591

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	14	114.8	70 to 130 %	Pass	13	107	70 to 130 %	Pass	7.4	<=25	Pass
cis-1,2-Dichloroethylene	12	13	108.3	70 to 130 %	Pass	12	100	70 to 130 %	Pass	8.0	<=25	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	14	116	70 to 130 %	Pass	0.0	<=25	Pass
1,2-Dichloroethane	12.1	11	90.9	70 to 130 %	Pass	11	90.9	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethene	12.3	14	113.8	70 to 130 %	Pass	13	106	70 to 130 %	Pass	7.4	<=25	Pass
Tetrachloroethylene	12.2	12	98.4	70 to 130 %	Pass	9.6	78.7	70 to 130 %	Pass	22.2	<=25	Pass
1,1,1-Trichloroethane	12	12	100.0	70 to 130 %	Pass	11	91.7	70 to 130 %	Pass	8.7	<=25	Pass

Test 6

Exposure Time: 162 seconds (2.70 minutes)

Baseline Sample ID: 01W7593

Test Sample ID: 01W7596

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	13	106.6	70 to 130 %	Pass	13	107	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	12	100.0	70 to 130 %	Pass	13	108	70 to 130 %	Pass	8.0	<=25	Pass
1,1-Dichloroethane	12.1	13	107.4	70 to 130 %	Pass	14	116	70 to 130 %	Pass	7.4	<=25	Pass
1,2-Dichloroethane	12.1	10	82.6	70 to 130 %	Pass	11	90.9	70 to 130 %	Pass	9.5	<=25	Pass
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	14	114	70 to 130 %	Pass	7.4	<=25	Pass
Tetrachloroethylene	12.2	9.8	80.3	70 to 130 %	Pass	9.5	77.9	70 to 130 %	Pass	3.1	<=25	Pass
1,1,1-Trichloroethane	12	12	100.0	70 to 130 %	Pass	11	91.7	70 to 130 %	Pass	8.7	<=25	Pass

Table 1  
RESULTS SUMMARY FROM

TEST PLAN FOR THE EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS

Test 7

Exposure Time: 329 seconds (5.48 minutes)

Baseline Sample ID: 01W7589

Test Sample ID: 01W7590

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	13	106.6	70 to 130 %	Pass	13	107	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	13	108.3	70 to 130 %	Pass	13	108	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	14	116	70 to 130 %	Pass	0.0	<=25	Pass
1,2-Dichloroethane	12.1	11	90.9	70 to 130 %	Pass	11	90.9	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	13	106	70 to 130 %	Pass	0.0	<=25	Pass
Tetrachloroethylene	12.2	9.1	74.6	70 to 130 %	Pass	9.5	77.9	70 to 130 %	Pass	4.3	<=25	Pass
1,1,1-Trichloroethane	12	12	100.0	70 to 130 %	Pass	12	100	70 to 130 %	Pass	0.0	<=25	Pass

## **CENTRALIZED CONFIRMATION FACILITY TIME-MOTION-DOSE STUDY**

# Time-Motion-Dose Study

(this is Goff Word file/CWC/CWC Time-dose Position paper)

Prepared by Tom Goff \_\_\_\_\_ / \_\_\_\_ / \_\_\_\_  
Print Signature Date

Reviewed by \_\_\_\_\_ / \_\_\_\_\_ / \_\_\_\_\_  
Print Signature Date

Approved by \_\_\_\_\_ /\_\_\_\_\_/\_\_\_\_\_  
 Print Signature Date

## Summary

This position paper provides documentation of the evaluation and estimation of personnel exposures from the characterization confirmation process for transuranic wastes at the Waste Isolation Pilot Plant (WIPP). This estimate is required for the ALARA Design Review and for the revision to the WIPP Contact Handled Waste Safety Analysis Report. Three primary work groups were estimated: Centralized Characterization Confirmation Facility workers (CCF); Waste Handling Personnel (WHO) and radiological control technicians (RCT).

The total estimated exposures for the three primary work groups associated with waste characterization are summarized in Table 1.

<b>Table 1</b>							
<b>Summary of Estimated Exposures for Waste Characterization At WIPP</b>							
Task	Estimated Dose (person-mrem/drum)			Number Drums/ year	Estimated Annual Dose (person-mrem)		
	CCF	WHO	RCT		CCF	WHO	RCT
Generate 7 & 4 drum Packs and transfer between CH Bay, OPRR & TMF	0.00	0.42	0.02	2500	0	1041	60
Perform gamma, neutron counting and RTR	0.13	0.42	0.00	2500	313	1041	0
Perform head space gas sampling	0.12	0.01	0.02	2500	298	36	39
Transfer RCRA pallets from Overpack and Repair room to site generated waste room	0.00	0.01	0.00	25	0	0	0
Prepare and Bag on and Bagoff Parent Drum	4.09	0.00	0.36	25	102	0	9
Perform visual exam	20.55	0.00	1.17	25	514	0	29
Attach and Remove Output drum	4.44	0.00	0.25	50	222	0	13
Return RCRA pallet from site generated waste room to Overpack and repair room	0.00	0.01	0.00	25	0	0	0
Total Exposure per group (person-rem)					1.448	2.118	0.149
Total Characterization Exposure (person-rem)						3.715	

This study uses a methodology that results in a collective dose per drum estimate. This methodology was chosen to allow easy adjustments of the estimated dose based on changes to the number of drums being handled through the waste characterization confirmation and for changes to the requirements for confirmation. For example, two output drums are assumed for each drum visually examined; this was assumed as the volume of material will increase as all the internal packages are unwrapped and additional materials added from cleaning the inside of the glovebox. The doses associated with changes in these assumptions can easily be determined using this methodology.

The tasks shown above will be performed by multiple workers in the specified groups. Therefore, no single individual should approach administrative exposure limits from this work.

It should be emphasized that this is a preliminary estimate of the potential doses associated with waste characterization confirmation at WIPP. The equipment and procedures for confirmation were still in the process of being purchased and developed as this evaluation was being conducted. While this may result in some potential errors in the dose estimates, any inaccuracies in the time and motion estimates should lie within the errors associated with the exposure rate estimates due to the variability of the source term of wastes arriving at WIPP. The Baseline Inventory Report data represents the average of all contact handled (CH) wastes expected at WIPP. Individual drums and site average wastes can, and will, vary from this average by several orders of magnitude in concentration and dose rate.

This evaluation should not be used for specifying radiological controls or dosimetry requirements. Individual drums of waste could have exposure rates 100's of times the averages assumed for this evaluation. In addition, changes in processes and requirements could have significant impact on these estimates as the process continues. Specific controls and dosimetry requirements will be specified by the ALARA Job Review for tasks in waste characterization. Based on this evaluation, suspension limits will be specified which will require shifting to RWPs with additional controls and dosimetry requirements.

This preliminary estimate of exposures may be used as a benchmark for optimization evaluations for changes to the waste characterization confirmation processes and facilities. The development of this estimation also provided an opportunity for the incorporation of ALARA optimization considerations during the early design phase of the project as required by 10 CRF 835.1002, Facility Design and Modifications.

## Purpose

This paper estimates the increased exposures to WIPP personnel due to waste characterization confirmation work at the Waste Isolation Pilot Plant. This evaluation is required for the Safety Analysis Report revision and the ALARA Design Review for waste characterization confirmation at the WIPP site.

## Background

Waste characterization is required by the WIPP RCRA permit. The WIPP Safety Analysis report must be revised to document the evaluation of the new activities and hazards associated with the processes used to characterize wastes prior to disposal in the underground. Part of the revision to the SAR should include an update to the dose estimate for Contact Handled (CH) waste handling based on the increased doses associated with waste characterization confirmation activities.

10 CFR 835, Subpart K, Design and Control<sup>1</sup>, requires that facility designs and modifications be made such that exposures to radiation and radioactive materials are as low as reasonably achievable. Section 704, Administrative Records, requires that ALARA actions in "...facility design and control actions required [by Subpart K]....be documented." The instrument used to document ALARA design reviews is specified in WIPP 12-2, ALARA Program Manual, Attachment 2, ALARA Design Review Checklist. In addition, to the checklist a dose assessment of the process is listed as a phase of the ALARA design review by the DOE Occupational ALARA Program Guide<sup>2</sup>.

## Analysis

The dose estimate is based on the sum of the estimated exposures for the various tasks involved in waste characterization confirmation. Exposure rate gradients were estimated using Microshield®. The source terms were based on the average isotope inventory and matrix stated in the Baseline Inventory Report<sup>3</sup>. Six source geometry's were assumed for the exposure rates to the workers involved in waste characterization: 1) Single 55 gallon drum; 2), 14 pack of drums; 3), 4 drums in a RCRA pallet; 4), 7 pack of drums; 5), contact and 6), arm exposure rates inside gloveboxes.

The glovebox dose rates were determined with Microshield® with a source term based on the volume of a 55 gallon drum of CH waste matrix distributed over the floor of the glovebox. Two evaluations were conducted. The contact photon dose rate at the center of the glovebox and for the dose rate at the side of the glovebox. The dose rate at the side of the glovebox was used to estimate the whole body dose rate. This is considered conservative as the arm whole body region has a compartment factor<sup>4</sup> of 0.005 making dose to the shoulder (Thorax; compartment factor 0.38) more limiting to the whole body than the elbow.

The dose equivalent rate is assumed to equal the exposure rate determined by Microshield®. This assumption is based on the evaluation of two exposure rate determinations for CH waste. Table 2 summarizes these comparisons. The exposure

rates contributing greater than 1% of the total were corrected to the dose equivalent rates using the ICRP rem/Roentgen<sup>5</sup>. The sum of the dose equivalent rates were then compared to the sum of the exposure rates. In both cases, the dose equivalent rates were less than the respective exposure rates. Based on these examples, use of the exposure rate for dose equivalent rate is conservative.

Table 2					
Comparison of Dose Equivalent to Exposure from CH Wastes					
Photon Energy (MeV)	rem/R	Contact Inside Glovebox mR/hour >1%	Contact Inside Glovebox mrem/hour	55 Gallon Drum @ 40cm mR/hour >1%	55 Gallon Drum @ 40cm mrem/hour
0.06	1.20	0.90	1.08	0.15	0.18
0.10	1.25	0.01	0.01	-----	-----
0.20	1.05	0.01	0.01	-----	-----
0.30	1.00	0.03	0.03	-----	-----
0.60	0.90	11.70	10.53	-----	-----
0.66	0.90	-----	-----	6.90	6.21
0.80	0.90	0.02	0.02	-----	-----
1.00	0.90	0.20	0.18	-----	-----
1.17	0.90	-----	-----	0.14	0.13
1.33	0.90	-----	-----	0.15	0.14
1.50	0.90	0.30	0.27	0.08	0.07
	sum	13.17	12.13	7.42	6.72

The exposure rates for a 14 pack of CH are summarized in Appendix 1. The 14 pack estimate was performed for the re-determination of doses for MgO use<sup>6</sup> and the data package for the Microshield® evaluation is maintained with that study. The dose rate for a 7 pack is estimated to be ½ of a 14 pack. This dose rate is valid as the 14-pack estimate is based on the fluence at the mid-point between the 2 –7 packs. Removing ½ the source term will reduce the dose rate by a factor of 2 along a line radially out from the mid-point of the 14 pack. This corresponds to point of interest for the dose to the worker. The abdomen has the highest compartment factor of all body locations. From a 7 pack, the dose below the abdomen will be corrected by a compartment factor of 0.005. Dose above the waist (1 drum height) will be decreasing from the dose rate estimated by the model. Therefore, use of ½ a 14 pack can be considered conservative .

The dose rates from a single 55 gallon drum are summarized in Appendix 2. The output from the Microshield® evaluation is maintained with the file copy of this position paper . The 55 gallon drum geometry is based on the BIR waste matrix materials density and isotope mixture. The volume was adjusted to account for the drum ribs.



A comparison of the 14 pack and single drum dose rate gradient indicates that the contact dose rate is higher for the 55 gallon drum than for the 14 pack. This is because the source model used for the 14 pack combines the Standard Waste Box with a 14 pack geometry adjusted for the void volume around the drums in the 14 pack. Care should be exercised when using the 14 pack model for estimating doses at close distances from the source because of this combination. This estimate uses the 14 pack dose rate only at 8 feet and this value lies outside the distance where the geometry averaging is expected to generate significant errors.

The 4 drum RCRA Pallet dose rate gradient is summarized in Appendix 3. This dose rate gradient was estimated using the BIR waste matrix materials and isotope mixture but were adjusted for a density change to account for a volume assumption to correct for using a rectangular source geometry to model the 4 – 55 gallon drums. The outside perimeter for the source was assumed to equal the outside of the 55 gallon drums on the pallet. The mass of waste in the 4 – 55 gallon drums were then adjusted by the volume of the source model and the new density was used for the waste material density and isotope concentration. This adjustment was made to provide a better estimate of the dose rate gradient from contact with the drums.

The dose rates for work inside gloveboxes are summarized in Appendices 4 and 5. The source term for the Microshield® evaluation is the contents of one 55 gallon drum distributed over the bottom of a glovebox. The source is based on the BIR waste matrix materials density and isotope mixture. The dose to the whole body from glovebox work is assumed to be at the side of the glovebox and no credit is taken for the glovebox materials as the shoulder will be at the opening into the glovebox. This geometry is summarized in Appendix 5.

The dose to the extremities is based on the same source configuration as the glovebox side geometry but at a point ½ inch from the source in the center of the glovebox. This geometry is summarized in Attachment 4.

The output from all the Microshield® evaluations for this paper, other than for the 14 Pack, are maintained with the file copy of this paper.

In addition, an evaluation of potential beta dose rates through gloves from anticipated isotopes in CH waste was conducted using VARSKIN. VARSKIN is a software package that allows determination of beta dose rates from various sources through varying air and material gaps. VARSKIN was developed for DOE by Pacific Northwest Laboratories<sup>7</sup> and is used throughout the nuclear industry for determination of beta skin doses. VARSKIN is also specified for use in determining beta skin doses at WIPP

The VARSKIN evaluation was conducted for 30 mil gloves with a beta source consisting of significant beta emitters at concentrations indicated in the Baseline Inventory Report. The conclusion of the evaluation, as shown in Appendix 6, is that the average beta dose rate through 30 mil gloves would be approximately 18 mrem/hour. While this is a very low dose

rate, it shows that beta radiation could cause skin exposure to personnel performing visual exams. As the actual source term could vary from the assumed average by several orders of magnitude, monitoring of the hand directly (i.e., rings) may be required. Use of thicker or leaded gloves could reduce the beta radiation levels, making ring badges unnecessary.

### Estimate for Generation and Handling of RCRA Pallets

The generation and handling of the RCRA pallets involves several tasks which were segregated based on information on the duration of each task and the possibility that each task may not be performed on every drum. The tasks, estimated time duration's and estimated exposures are summarized in Table 3.

<b>Table 3</b>								
Generate 4 and 7 Packs and Transfer to/from TMF								
Data Source: MoO Video Tape and LANL Time Study								
Step	# of Workers	Worker type	Average Distance (feet)	Time Start	Duration (min)	Dose Rate (mrem/h)	Dose (person-urem / drum)	Comments
Separate 14 pack into 2 - 7 packs	2	WHO	8	06:15	3.25	2	15	MGO tape: 14 pack dose rate
Survey newly exposed surefaces	1	RCT	2	n/a	2	5	12	
Move 7 Pack to Overpack & Repair Room	1	WHO	6	n/a	6	3	21	Time from LANL-C study
Separate 7 pack into 4 drum RCRA Pallets	1	WHO	6	n/a	30	3	107	"
Survey newly exposed surfaces	1	RCT	2	n/a	2	5	12	
Move RCRA pallet through airlock to WHB	1	WHO	6	n/a	6	1.2	30	Exposure rate for 4 drum RCRA Pallet
Move RCRA pallet through airlock to TMF	1	WHO	6	n/a	6	1.2	30	
Return RCRA pallet to Overpack and Repair Room	1	WHO	6	n/a	12	1.2	60	
Generate 7 Pack from RCRA Pallet	1	WHO	6	n/a	30	1.2	86	Assume time equal to breakup to 4 packs
Move 7 Pack to CH Bay	1	WHO	6	n/a	6	3	43	Assume time equal to move from CH bay
<b>Dose Totals</b> (Person-urem/drum)	CCF 0		WHO 416		RCT 24		Total 440	

In this and other tables where video tape segments are not available, the "Time Start" column is not applicable. Time start and time End is applicable to durations which are traceable to video tape segments. As these tables will be updated in the future the columns are left in place. Instead of Time Stop, the estimated duration of each task is listed.

The time and distances for the separation of a 14 pack into 2 - 7 packs is based on a video segment of the separation process made on 8/25/2000. The "Time Start" is shown

to provide traceability to the video tape location for validation. The exposure was based on 2 workers working a average of 8 feet from a 14 pack of drums. While the drums are about 6 feet from the operator during transport, 8 feet is used to account for the time the drums are away from the pallet and further from the operator.

The time associated with movement of each 7 pack to the Over Pack and Repair Room (OPRR) are based on a study obtained from Los Alamos National Laboratory – Carlsbad<sup>8</sup>. Normal forklift operations are assumed where the operator will be about 6 feet from the drums. Only one worker is assumed as the spotter can stay away from the waste drums if exposure rates are significant.

The time associated with the separation of 7 packs to 4 drum RCRA pallets is given in the LANL study<sup>8</sup>. A worker distance of 6 feet is used as most time will be using the single drum handling unit.

Times for movements of the 4 drum RCRA pallets through airlocks are from the LANL study<sup>8</sup>. Exposure rates for the 4 packs were calculated with Microshield® using a rectangular volume based on the outer perimeter of 4 drums. The total activity was held constant and the waste matrix density and isotope concentrations were reduced to account for the increased volume. The exposures estimated are shown in Appendix 3.

## **Estimate for Non-Invasive Characterization Activities**

Non-invasive characterization activities involve radiography, gamma spectral tomography and neutron counting. These tasks determine the radiolytic and physical composition of the matrix in the drum.

A time of 6 minutes is assigned for each drum move. This is the standard time for a movement of drums in the LANL study<sup>8</sup>. Five minutes is assumed to allow operators to position the drums in each of the NDE units. No dose is assumed for the operators after the drums are in the examination/detection cells because of the shielding and distance to the operator stations. This assumption will be validated by radiation surveys when the equipment is started up.

A single 55 gallon drum exposure rate gradient is used for the dose estimations. The calculated exposure rates are shown in Appendix 2. The personnel doses for non-invasive activities are summarized in Table 4.

Table 4								
Task Description: Perform Non-destructive Exams in TMF								
Data Source: LANL Time Study								
Step	# of Workers	Worker type	Average Distance (feet)	Time Start	Duration (min)	Dose Rate (mrem/h)	Dose (person-urem / drum)	Comments
Move drum onto/out of RTR Unit	1	WHO	6	n/a	10	1	12	Single drum dose rate
Operator load/unload drum for RTR	1	CCF	2	n/a	5	7	42	Single drum dose rate
Move drum from RTR Unit to Gamma Tomography unit	1	WHO	6	n/a	10	1	12	
Operator perform Gamma Tomography	1	CCF	2	n/a	5	7	42	
Move drum from Gamma Tomography unit to Pasive Neutron Counter	1	WHO	6	n/a	10	1	12	
Operator perform Passive Neutron Counting	1	CCF	2	n/a	5	7	42	
Dose Totals	CCF		WHO		RCT		Total	
(Person-urem/drum)	125		36		0		161	

### Estimation for Head Space Gas Sampling

Head space gas sampling will be conducted in the Over-pack and Repair Room (OPRR). Movements of drums between the TMF and the OPRR are included in the times-doses for Generation and Handling of RCRA Pallets. A single drum exposure rate was used for the exposure estimate. Drum positioning is estimated at 5 minutes.

Times for other activities are based on discussions with personnel involved in waste characterizations and will be refined as actual equipment becomes available during system startups at WIPP. Errors associated with this assumption are expected to lie within errors associated with use of the average waste matrix and isotope mixtures used in the development of the exposure rate terms.

The personnel doses for headspace gas sampling are summarized in Table 5.

<b>Table 5</b>								
Task Description: Perform Head Space Gas Analysis								
Data Source: LANL Study for drum movements								
Step	# of Workers	Worker type	Average Distance (feet)	Time Start	Duration (min)	Dose Rate (mrem/h)	Dose (person-urem / drum)	Comments
Move drum to Head Space Gas unit	1	WHO	6	n/a	6	1	7	
Position drum at sample location	1	CCF	2	n/a	5	7	42	
Position exhaust hood and Insert needle	1	CCF	1	n/a	2	13	31	
Remove Sample needle	1	CCF	1	n/a	1	13	15	
Gross survey sample needle	1	RCT	1	n/a	1	13	15	
Remove drum vent filter	1	CCF	1	n/a	1	13	15	
Install new drum filter	1	CCF	1	n/a	1	13	15	
perform contamination survey drum top	1	RCT	1	n/a	2	13	31	
Return drum from Head Space Gas to RCRA pallet	1	WHO	6	n/a	6	1	7	
<b>Dose Totals</b>	CCF		WHO		RCT		Total	
(Person-urem/drum)	119		14		15		149	

### Exposure Estimation for Visual Examination

There are 4 tasks evaluated for the visual examination process: 1) Transfer of drums to be characterized to and from the visual exam facility; 2) Preparing, bagging on and off the parent drum for opening in the glovebox; 3) performing visual exams of drum contents, and 4) bagging on and off of output drums.

Transfer of drums to and from the visual exam facility is considered to have the same exposures as transfer of drums through the airlocks to and from the TMF and OPRR. The exposure associated with moving drums to and from the visual exam facility are separated from other characterization activities as not all drums will be visually examined.

The personnel exposures estimated for preparing, bagging on and bagging off drums for visual exam are summarized in Table 6. The times and personnel distances from sources are based on a video taken at Nevada Test Site of waste characterization activities. The times shown on Table 6 match the times on the tape. The exposure rates are based on a single 55 gallon drum of CH waste. The times, personnel distances and estimated doses are summarized in Table 6.

<b>Table 6</b>								
Task Description: Prepare/Sleeve bagon/bagoff Parent Drum								
Data Source: Nevada Test Site Video								
Step	# of Workers	Worker type	Average Distance (feet)	Time Start	Time Stop	Dose Rate (mrem/h)	Dose (person-urem / drum)	Comments
Remove Seal and loosen bolt from drum	1	CCF	1	1001	1003	13	433	
Install Sleeve	2	CCF	2	1003	1005	4	267	
Seal tape/check sleeve	1	CCF	1	1005	1006	13	217	
Sleeve in uncharacterized drum to glovebox	2	CCF	1	1330	1337	13	3033	
monitor sleeve in	1	RCT	3	1330	1337	3	292	
Backout drum/ makeup and cut pigtail	2	CCF	8	1322	1329	1	140	Distance from filled output drum located under glovebox
	1	RCT	8	1322	1329	1	70	
<b>Dose Totals</b> (Person-urem/drum)	CCF		WHO		RCT		Total	
	4090		0		362		4452	

The exposures estimated for visual examination are based on a video tape made at WIPP of MOVER visual exam on 12/20/2000. The times indicated in the tables match the time stamps on the video tape. The geometry's associated with exposures to personnel directly handling the wastes are much more complex and variable than those associated with handling wastes inside drums. Several different geometry's and points of exposure are utilized in this exposure estimate.

The exposure during the lid removal is assumed to be solely from the drum being opened. While the workers hands are in direct contact with the drum, the elbow exposure is assumed to be 1.7 feet from the source. Once the drum is lid is removed, all exposures are assumed to be on "contact" with the wall of the glovebox as shown in Appendix 5. The assumption that the only source will be the drum being opened is based on ALARA considerations. If the output drum has significant dose rates, it will be removed before the in-processing of another drum begins.

Appendix 4 shows the estimation of the exposure rate on contact with CH waste distributed over the bottom of the glovebox. Contact exposure rate is estimated as 25 mR/hour or approximately 2 times that expected to the elbow. While this might be inferred to mean that monitoring of the extremities is not required for visual examinations, this issue will require further evaluation. This evaluation will have to include the variability of potential sources and the possibility of beta exposures. This evaluation will be conducted as part of the ALARA Job Review required for the RWP for visual examination.

The times, relative positions and estimated exposures for the various tasks of visual exam are summarized in Table 7.

<b>Table 7</b>								
<b>Perform Visual Exam</b>								
Data Source: WIPP Video of MOVER Operations 12/20/2001								
Step	# of Workers	Worker type	Average Distance (feet)	Time Start	Time Stop	Dose Rate (mrem/h)	Dose (person-urem / drum)	Comments
Unbolt and Remove lid in glovebox	2	CCF	Side	1001	1003	14	933	Dose to Shoulder of worker
Unload and number drum contents	2	CCF	Side	1004	1009	14	2333	Dose to Shoulder of worker
RCT survey of drum contents	1	RCT	Side	1004	1009	14	1167	Dose to Shoulder of worker
Close drum	2	CCF	8	1009	1010	0.5	17	Assume GB empty; dose from output drum
Calibrate Balance	2	CCF	1	1013	1017	0	0	Assume GB empty & no parent/output drums
Open bags, Perform inventory of contents	2	CCF	Contact	1018	1055	14	17267	Exposure rate to elbow of worker; drum contents on floor of GB.
<b>Dose Totals</b>	CCF		WHO		RCT		Total	
(Person-urem/drum)	20550		0		1167		21717	

## Handling of Output Drums

The attaching and removal of visual examination output drums is evaluated separately as there may be a larger number of output drums than parent drums. Exposure rates are based on a single 55 gallon drum of waste. During bag on of an output drum the source is a full parent drum. When bagging off the output drum it is considered to be the source.

The personnel geometry's, source intensities and resultant exposure estimates are summarized in Table 8.

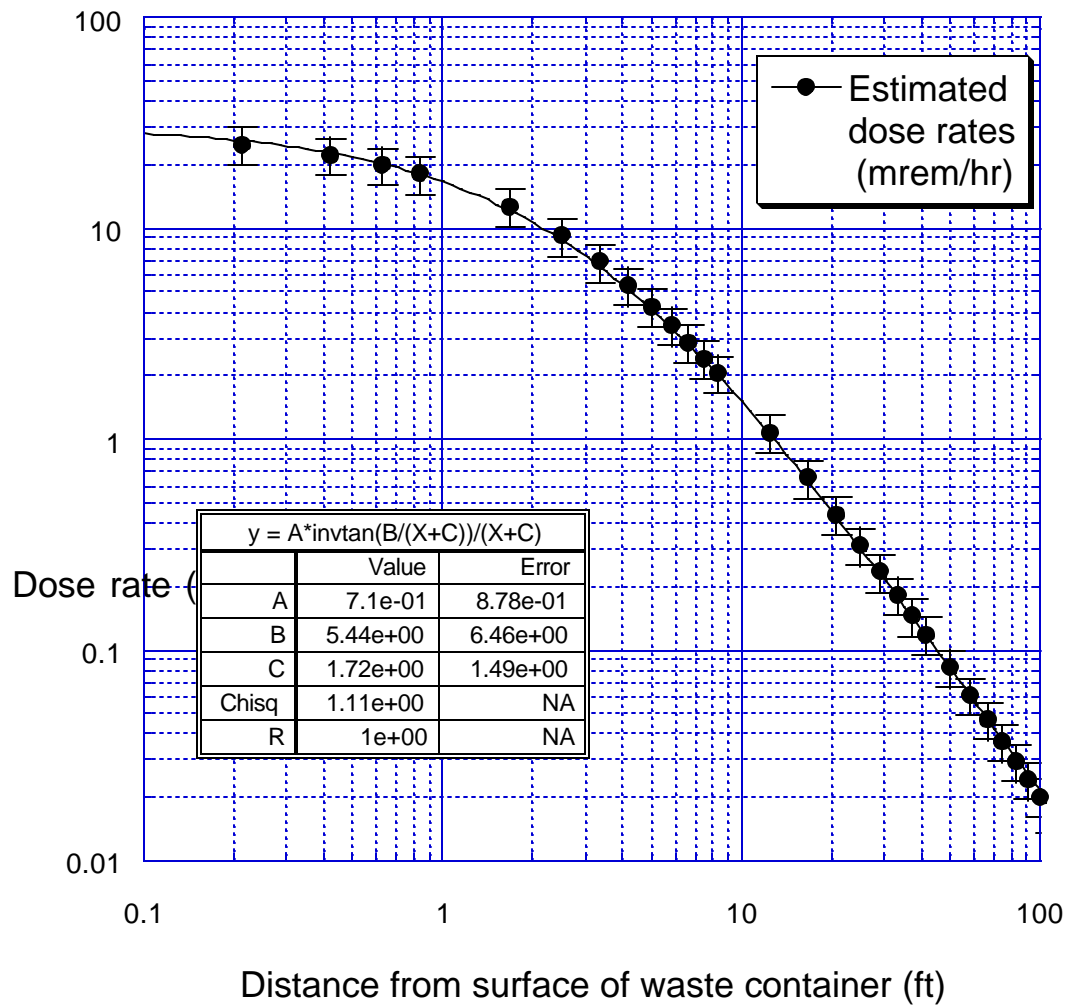
<b>Table 8</b>								
Task Description: Attach and remove Outlet Drum at bottom of Glovebox								
Data Source: WIPP Video of MOVER Operations 12/20/2000								
Step	# of Workers	Worker type	Average Distance (feet)	Time Start	Time Stop	Dose Rate (mrem/h)	Dose (person-urem / drum)	Comments
Attach drum to bottom of glovebox	2	CCF	8	1354	1358	0.8	107	Distance from filled parent drum located @ bagon point
RCT monitor work	1	RCT	8	1354	1358	0.8	53	
Wipe down drum sleeve/moisten bag	2	VE	1	1120	1122	13	867	
Crimp up, Tape and cut Pigtail	2	CCF	1	1122	1128	13	2600	
Put on lid, roll drum away from glovebox	2	CCF	1	1128	1130	13	867	removal during parent drum bagin
RCT Coverage	1	RCT	2	1128	1130	6	200	
<b>Dose Totals</b>	CCF		WHO		RCT		Total	
(Person-urem/drum)	4440		0		253		4693	

## Results

Estimated exposures from waste characterization processes at the WIPP are summarized in Table 1. This estimate is based on the best available source intensity, matrix and task times. This evaluation provides data which can be used for evaluation of further changes and possible conditions in the work place during waste characterization activities. This data provides indication of the approximate average exposures; actual exposures could be higher by several orders of magnitude for individual drums. Therefore, nothing in this estimate should be construed to limit radiological surveys or controls during waste characterization.

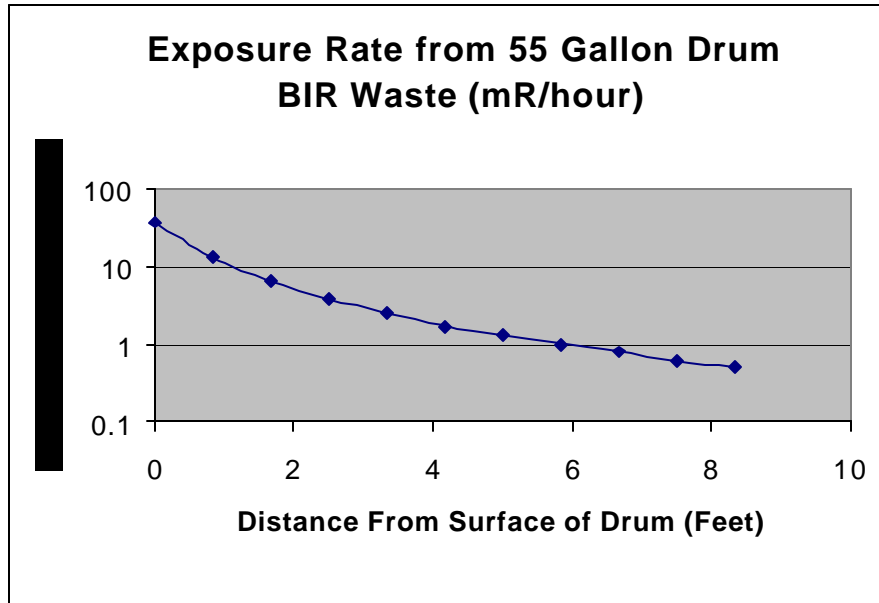


## Appendix 1 14 Pack Radial Dose Rate



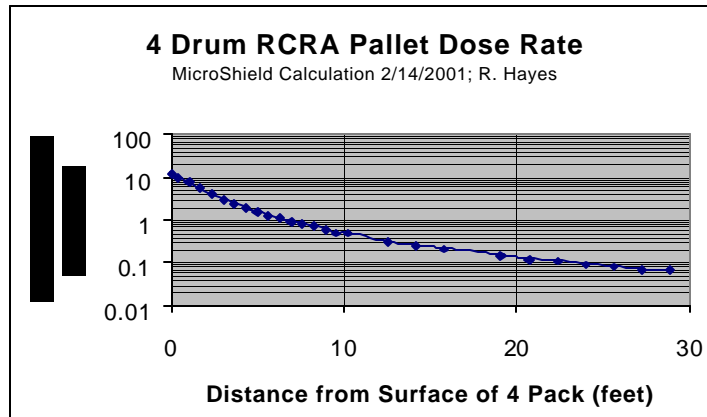
From Rad Con Position Paper 2000-07; Re-evaluation of MgO Emplacement Doses  
at WIPP

## Appendix 2



Distance from Center of Source (in)	Distance from Surface of Drum (feet)	Exposure Rate (mR/hour)
12	0	37
22	0.8	13
32	1.7	6.4
42	2.5	3.8
52	3.3	2.5
62	4.2	1.7
72	5.0	1.3
82	5.8	1.0
92	6.7	0.8
102	7.5	0.6
112	8.3	0.5

## Appendix 3



Distance from center of Source (cm)	Distance from Surface (feet)	Exposure Rate (mR/hour)
118.76	0	12.4
130	0.4	10
150	1.0	7.4
170	1.7	5.4
190	2.3	4
210	3.0	3
230	3.6	2.4
250	4.3	1.9
270	5.0	1.5
290	5.6	1.3
310	6.3	1.1
330	6.9	0.9
350	7.6	0.8
370	8.2	0.7
390	8.9	0.6
410	9.6	0.5
430	10.2	0.5
500	12.5	0.3
550	14.1	0.25
600	15.8	0.21
700	19.1	0.15
750	20.7	0.12
800	22.4	0.11
850	24.0	0.09
900	25.6	0.08
950	27.3	0.07
1000	28.9	0.07



## Appendix 5

### Exposure Rate At Side of Glovebox with 55 Gallon Drum of Waste Distributed Over Bottom of Glovebox

Case Title: Case 1  
Description: Case 1  
Geometry: 13 - Rectangular Volume

Source Dimensions

Length	8.636 cm	3.4 in
Width	274.32 cm	9 ft
Height	91.44 cm	3 ft

Dose Points

	X	Y	Z
# 1	10.16 cm	0 cm	137.16 cm
	4.0 in	0.0 in	4 ft 6.0 in

Shields

Shield Name	Dimension	Material	Density
Source	1.32e+04 in	Waste Matrix	5089
Air Gap		Air	0.00122

Source Input

Grouping Method : Standard Indices  
Number of Groups : 25  
Lower Energy Cutoff : 0.015  
Photons < 0.015 : Excluded  
Library : Grove

Results

Energy MeV	Activity photons/sec	Fluence Rate MeV/cm <sup>2</sup> /sec	Fluence Rate MeV/cm <sup>2</sup> /sec	Exposure Rate mR/hr	Exposure Rate mR/hr
		No Buildup	With Buildup	No Buildup	With Buildup
0.015	1.392e+03	1.971e-07	2.645e-07	1.691e-08	2.269e-08
0.02	7.455e+05	1.124e-03	1.778e-03	3.893e-05	6.158e-05
0.03	5.482e+08	4.202e-01	1.581e+00	4.165e-03	1.567e-02
0.04	5.244e+06	2.494e-02	1.184e-01	1.103e-04	5.234e-04
0.05	5.324e+06	7.189e-02	4.127e-01	1.915e-04	1.099e-03
0.06	7.637e+09	2.236e+02	1.468e+03	4.441e-01	2.917e+00
0.08	2.318e+06	2.119e-01	1.433e+00	3.354e-04	2.268e-03
0.1	2.206e+07	4.582e+00	2.856e+01	7.011e-03	4.369e-02
0.15	2.201e+05	1.714e-01	7.349e-01	2.823e-04	1.210e-03
0.2	1.958e+06	3.194e+00	9.814e+00	5.638e-03	1.732e-02
0.3	1.943e+06	6.957e+00	1.545e+01	1.320e-02	2.930e-02
0.4	3.648e+05	2.034e+00	3.863e+00	3.964e-03	7.527e-03
0.5	1.223e+05	9.283e-01	1.607e+00	1.822e-03	3.155e-03
0.6	3.274e+08	3.156e+03	5.132e+03	6.160e+00	1.002e+01
0.8	3.510e+05	4.867e+00	7.274e+00	9.257e-03	1.384e-02
1.0	3.346e+06	6.109e+01	8.680e+01	1.126e-01	1.600e-01
1.5	3.261e+06	9.692e+01	1.275e+02	1.631e-01	2.146e-01
2.0	1.509e+05	6.246e+00	7.878e+00	9.659e-03	1.218e-02
3.0	4.615e+05	2.990e+01	3.614e+01	4.057e-02	4.903e-02
TOTALS:	8.560e+09	3.597e+03	6.929e+03	6.976e+00	1.350e+01

## Appendix 6

### VARSKIN Analysis of CH BIR Beta Sources Through 30 mil gloves

(this is Goffword file/CWC/Beta dose)

B I R B e t a E m i t t i n g I s o t o p e s		
> 1 % of Y - 90 Activity and beta end point > 70 m a / c m <sup>2</sup> ( 0.300 M e V )		
I s o t o p e	A c t i v i t y u C i / c m <sup>3</sup>	B e t a E m a x ( M e V )
Y - 90	0.041	2.27
S - 90	0.041	0.546
C s - 137	0.048	1.176

#### VARSKIN Summary Program VARSKIN-MOD2 CH Beta Dose Through 30 mil glove Slab Source Geometry

Source Density : 1.000000 g/cm <sup>3</sup> X Side Length : 100000.000000 um Y Side Length : 100000.000000 um Thickness : 10000.000000 um Skin Depth : 7.000000 mg/cm <sup>2</sup>	Thickness of Cover : 7.60000E-01 mm Cover Density: 1.000000 g/cm <sup>3</sup> Air Gap Thickness : 25.400000 mm Irradiation Time : 60.000000 min
Nuclide : Sr-90 1.8*X90 Distance : 1.438200E-01 cm Average Beta Energy : 2.0140E-01 MeV	Source Strength : 4.1000E-02 uCi/cm <sup>3</sup> The beta dose rate averaged over 1.0square cm = 9.45E-05 rad/hr
Nuclide : Y-90 1.8*X90 Distance : 9.446400E-01 cm Average Beta Energy : 9.4800E-01 MeV	Source Strength : 4.0000E-02 uCi/cm <sup>3</sup> The beta dose rate averaged over 1.0000 square cm = 1.68E-02 rad/hr
Nuclide : Cs-137 1.8*X90 Distance : 2.757600E-01 cm Average Beta Energy : 2.3970E-01 MeV	Source Strength : 4.8000E-02 uCi/cm <sup>3</sup> The beta dose rate averaged over 1.0000 square cm = 1.19E-03 rad/hr

The beta dose rate for the 3 radionuclides = 1.81E-02 rad/hr

## References

---

<sup>1</sup> 10 CFR 835, Occupational Radiation Protection. 11/15/1999.

<sup>2</sup> DOE G441.1-2, Occupational ALARA Program Guide. US Department of Energy, 3/17/1999.

<sup>3</sup> Transuranic Waste Baseline Inventory Report. DOE/CAO-95-1121/Rev.3: US Department of Energy, Washington, DC. 1996.

<sup>4</sup> ANSI Standard N13.41, Criteria for Performing Multiple Dosimetry; This standard utilizes the concept of compartment factors. These factors are applied to dosimeter readings for various portions of the body to determine whole body dose equivalent. The use of N 13.41 is authorized in DOE G 441.1-4, External Dosimetry Program Guide. 1997

<sup>5</sup> ICRP 51, Data for Use in Protection Against External Radiation, Table 3b: Pergamon Press 1987...

<sup>6</sup> Re-determination of Doses for MgO Emplacement: WIPP Radiological Control Position Paper 2000-07; September 11, 2000.

<sup>7</sup> NUREG/CR-5853; PNL-7913; DP: VARSKIN MOD2 and SADDE MOD 2; Computer Codes for Assessing Skin Dose from Skin Contamination. Pacific Northwest Laboratory. Richland, Washington. November 1992.

<sup>8</sup> Waste Characterization Assumptions for Model: Los Alamos National Laboratory -Carlsbad; 9/11/2000.

**PIPE OVERPACK CONTAINER**



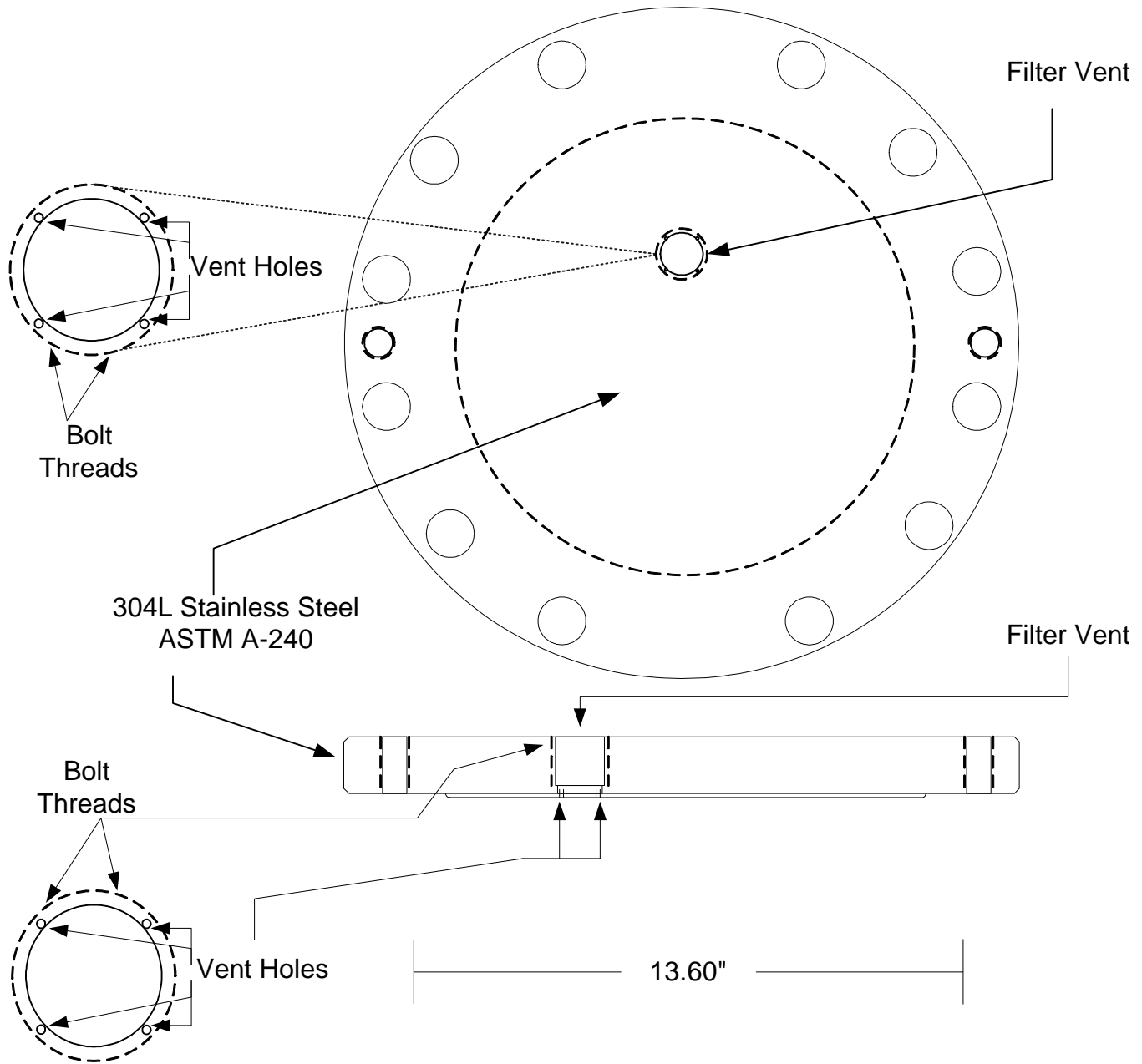
## Pipe Overpack Container

A pipe overpack container (POC) is a container which holds TRU waste and is subsequently overpacked into another container such as a 55 gallon drum.

The POC is designed such that there are only very limited connections between the waste and the filter vent hole. There are only four small holes (3/32 inch) in the plate that separates the filter vent hole from the headspace gas of the POC. It would be extremely difficult and time consuming to locate those holes with the headspace gas sampling apparatus inserted through a carbon composite filter. This activity would unnecessarily expose workers to undue radiation levels because of the time they would have to spend searching for one of the 3/32 inch holes.

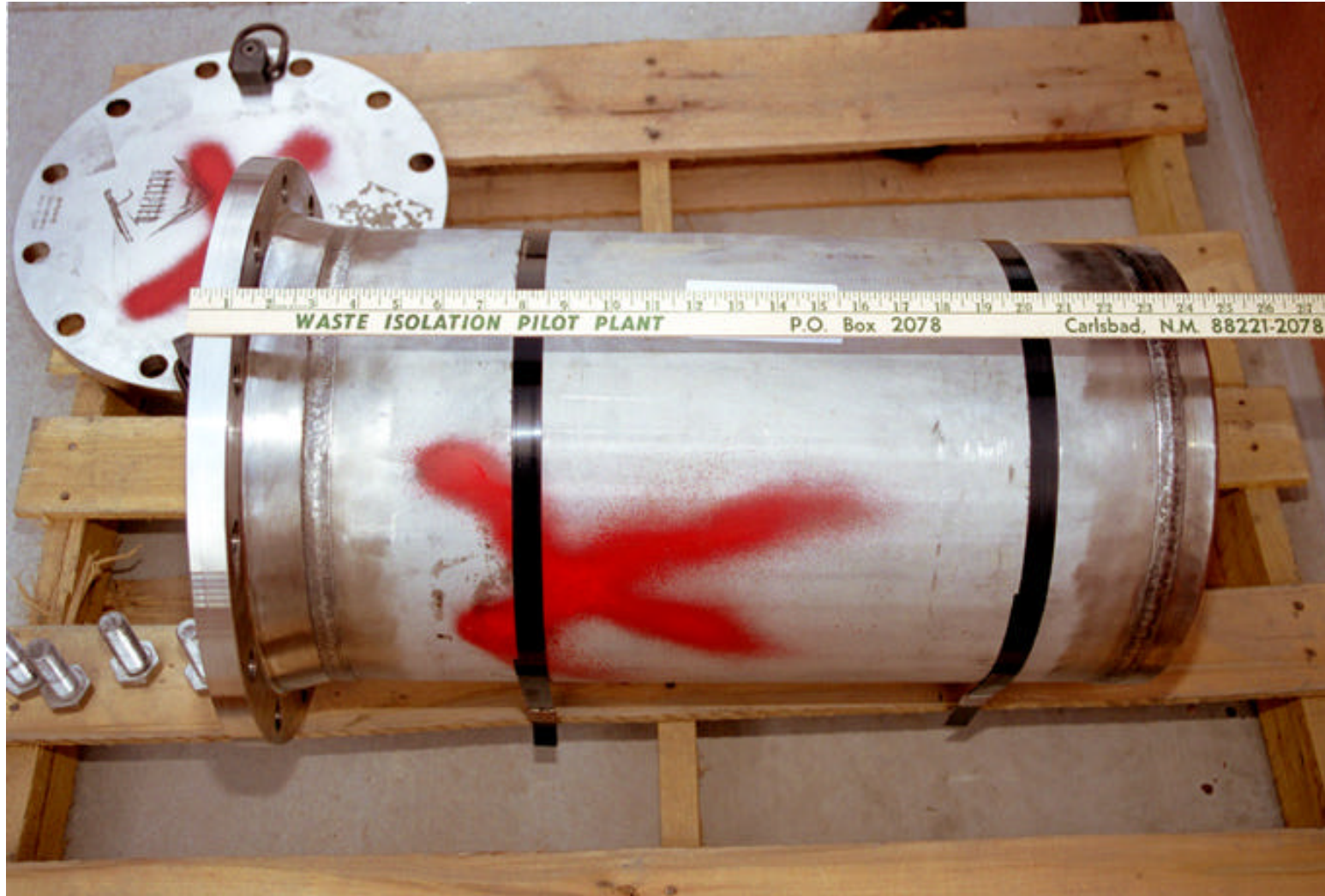
Photos and drawings of POCs are included in this section.

A report indicating that sampling through the existing filter vent hole has no impact on headspace gas concentrations is included as Attachment 4.

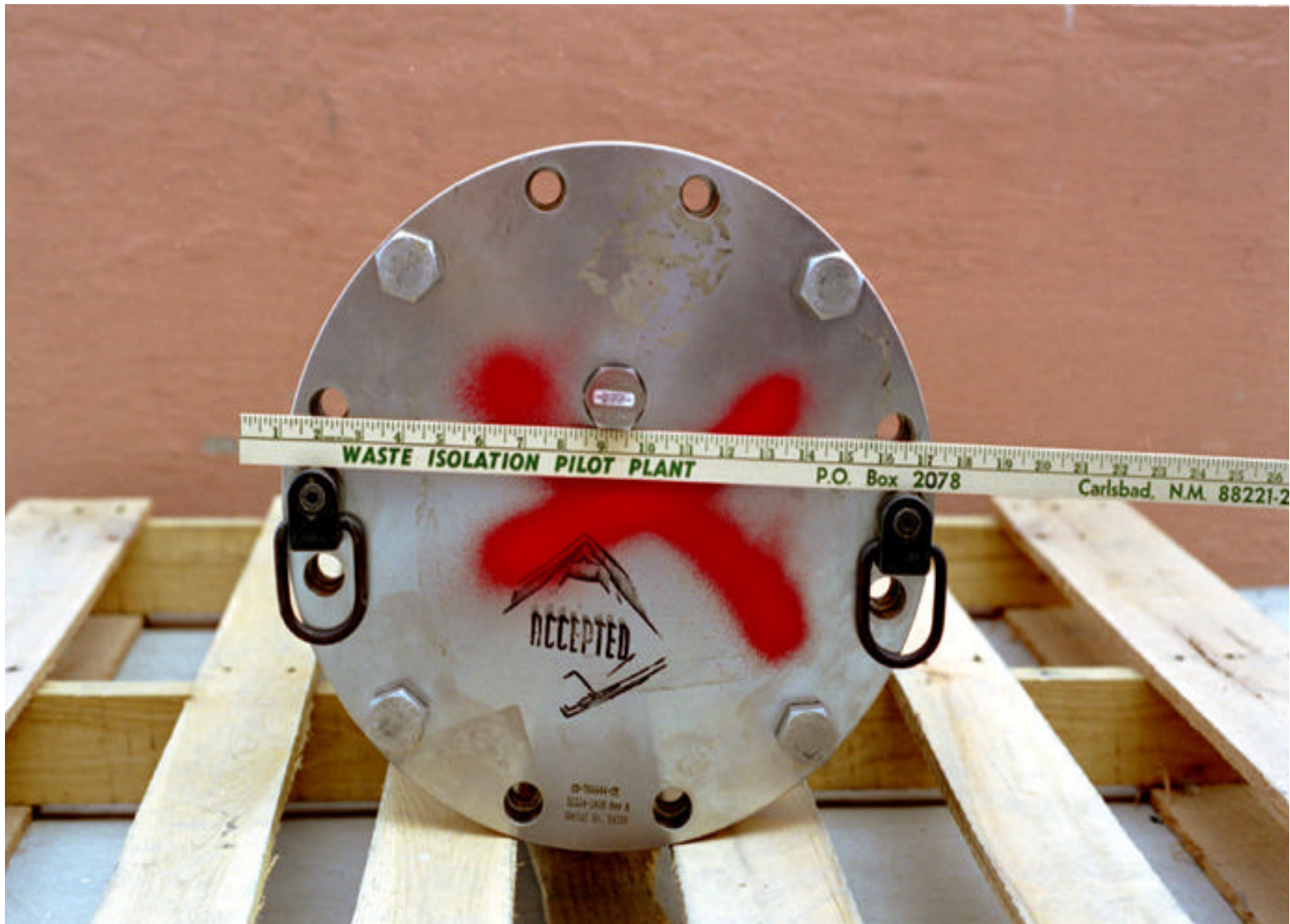


Not to Scale

Typical 12" Pipe Overpack Lid

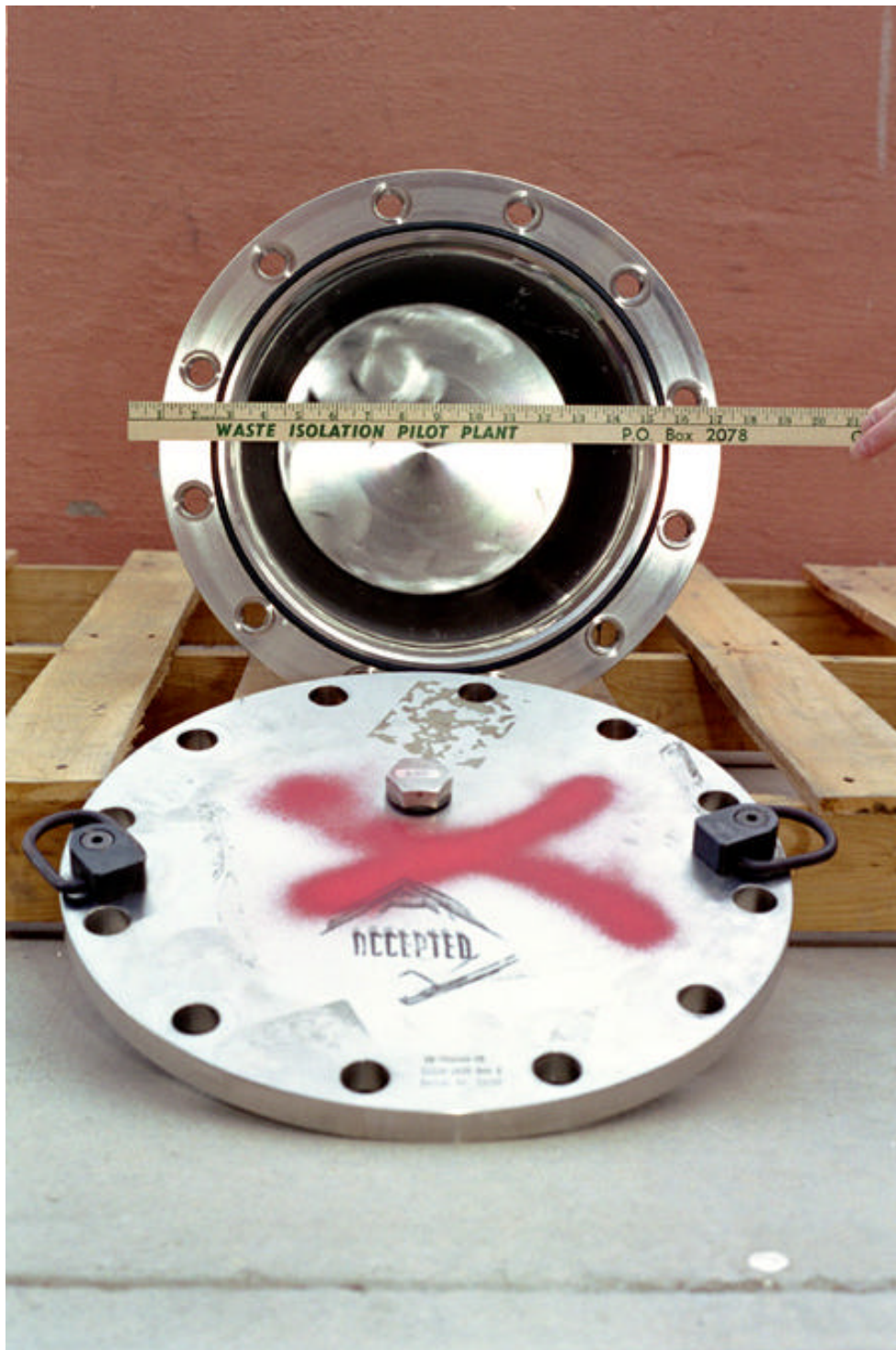


12" Pipe Overpack Body and Lid View



12" Pipe Overpack Lid View





12" Pipe Overpack Lid and Body Configuration

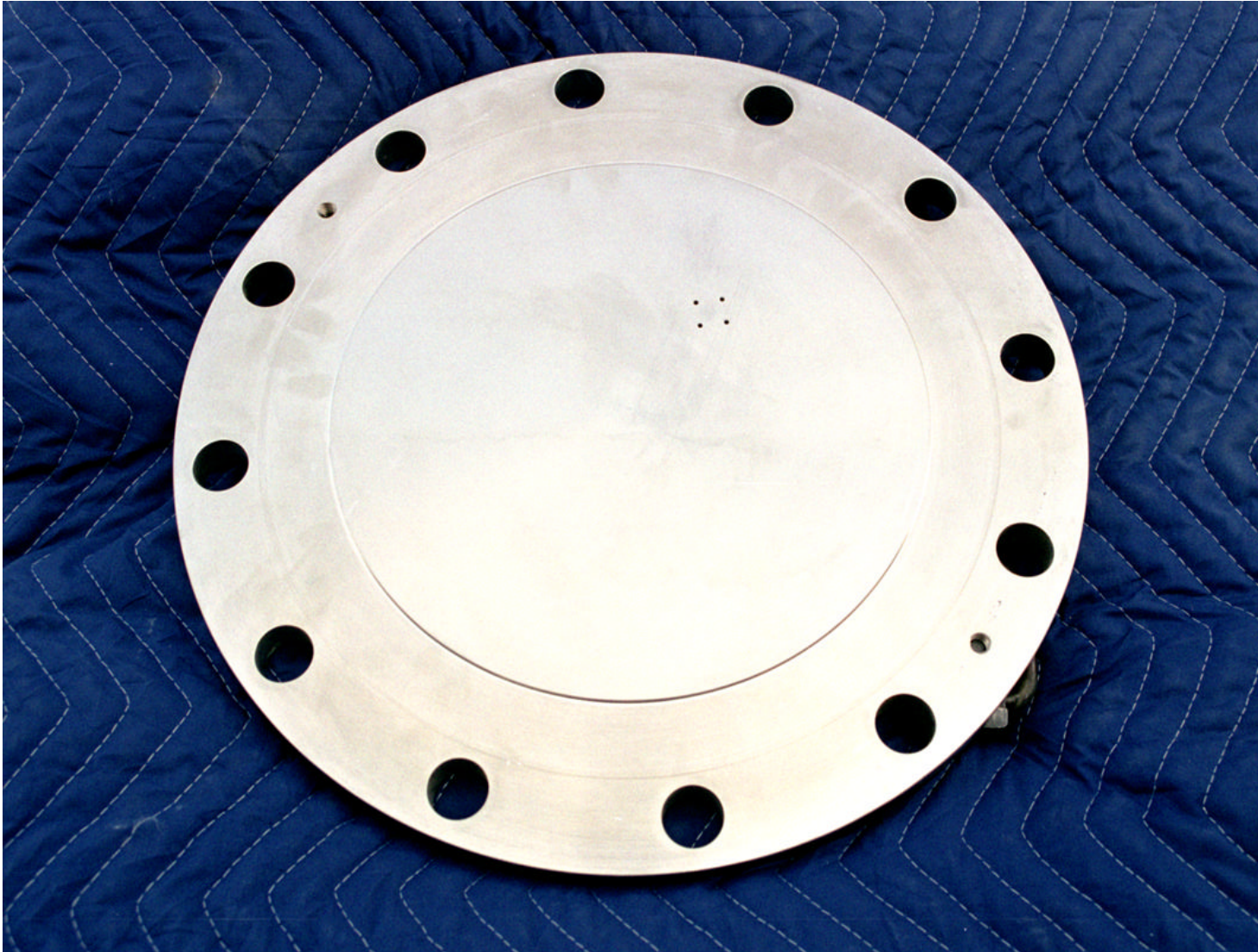


12" Pipe Overpack Lid- External View and Filter Plug



12" Pipe Overpack Lid - Filter Vent Plug





12" Pipe Overpack Inner Lid Surface View